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THE ACTION OF ZINC ON COPPER SILICIDE.

BY G. DE CHALMOT.

It was shown in previous articles that copper and silicon have only a feeble affinity for each other. The compound Cu_2Si is readily decomposed by many agents.

I have also communicated the fact that copper silicide can be decomposed by sulphur in such a manner that the silicon is obtained in free condition. I have looked for other reagents which will liberate the silicon from the copper without combining with it. It is not easy to find such reagents, for silicon, especially in *status nascendi*, is one of the most active substances. It is known, however, from the work of Vigoureux[1] that certain metals like zinc, tin, and aluminium do not unite with silicon. These metals readily form alloys with copper, and there was a possibility that their affinity for copper is greater than that of silicon.

I have actually found that zinc decomposes copper silicide, liberating the silicon. The reaction is a partial one. The more zinc there is present the more silicon there is separated from the copper.

This reaction is remarkable in so far as it shows that the affinity between the two metals, zinc and copper, is as great or greater than that between copper and silicon. Copper sili-

[1] Compt. rend., **123**, 115.

cide is undoubtedly a chemical compound, for the silicon in it is much more active than free silicon, being very readily oxidized. The copper in it does not dissolve in mercury and dissolves more easily in dilute acids than free copper. Vigoureux, moreover, obtained copper silicide in crystalline, pure condition. We may then take the reaction of the zinc with this copper silicide as additional evidence of purely chemical character in favor of the view that brass contains distinct chemical compounds.

The study of this reaction also seems to indicate that among the compounds, which copper and zinc form with each other, that compound which contains most copper has a composition not differing very far from the formula $ZnCu_2$. This result agrees with that of Charpy.[1] Neither tin nor antimony attacks copper silicide, which shows that they have less affinity for copper than zinc.

In carrying out the experiments the copper silicide was melted in a crucible, and the molten zinc was added. The mass was stirred and allowed to cool. A part of the zinc always burned up and often some silicon, as will appear from the following figures.

The silicon that is liberated is always crystalline. Probably it dissolves in the zinc or in the brass compounds and crystallizes on cooling. A silicide of the following composition was used :

Silicide No. 1.

	Per cent.
Cu	90.53
Fe	0.21
Si	9.26
Free Si	trace

or,

	Per cent.
Copper silicide : Cu_2Si	50.08
Free copper	49.62
Iron silicide	0.30

This silicide contains only traces of free silicon and very little iron, which facilitates the comparison of the results.

This silicide was mixed with increasing quantities of zinc amounting to ¼, ½, 1, 1½, 1¾, and 2 times the weight of the silicide.

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[1] Compt. rend., 122, 670.

The zinc which was used was 99.69 per cent. pure. It contained as impurities, besides some carbon, mainly iron. It was free of all metals that in acid solutions are precipitated by hydrogen sulphide. I assumed that the iron in the original silicide was united with one-half its weight of silicon. I further assumed that all the mixtures contained about 0.25 per cent. iron, which is derived partly from the silicide and partly from the zinc. It is improbable that the iron from the zinc should unite with the liberated silicon at the low temperatures which were used, hence I calculated it as being in the free condition. I made these assumptions to save many analyses and to help in the calculations. The quantities of iron are really so small that they cannot materially affect the result.

In the mixtures, copper, total silicon, and free silicon were determined. The amount of iron derived from the silicide was found by assuming that it varies in the same ratio as the copper. By subtracting this amount of iron from the assumed total amount of iron, 0.25 per cent., I found the amount of free iron derived from the zinc. The remainder of the sample, after deducting copper, silicon, and iron, was taken to be zinc. The following are the results obtained :

Experiment I.

1 part silicide, ¼ part zinc.

	Per cent.
Cu	72.56
Fe	0.25
Zn	20.04
Si	7.15
Free Si	trace

or,

	Per cent.
Copper silicide : Cu_2Si	38.66
Other copper	40.97
Iron silicide	0.24
Free iron	0.09
Zinc	20.04

Experiment II.

1 part silicide, ½ part zinc.

	Per cent.
Cu	61.92
Fe	0.25
Zn	31.73
Si	6.10
Free Si	0.99

or,

	Per cent.
Copper silicide : Cu_2Si	27.56
Other copper	39.40
Iron silicide	0.21
Free iron	0.11
Zinc	31.73
Free silicon	0.99

Experiment III.

1 part silicide, 1 part zinc.

	Per cent.
Cu	46.94
Fe	0.25
Zn	48.29
Si	4.52
Free Si	2.02

or,

	Per cent.
Copper silicide : Cu_2Si	13.40
Other copper	35.99
Iron silicide	0.15
Free iron	0.15
Zinc	48.29
Free silicon	2.02

Experiment IV.

1 part silicide, 1½ part zinc.

	Per cent.
Cu	38.90
Fe	0.25
Zn	57.52
Si	3.33
Free Si	2.88

or,

	Per cent.
Copper silicide : Cu_2Si	2.25
Other copper	37.06
Iron silicide	0.13
Free iron	0.16
Zinc	57.52
Free silicon	2.88

Experiment V.

1 part silicide, 1¾ part tin.

	Per cent.
Cu	35.34
Fe	0.25
Zn	61.23
Si	3.18
Free Si	2.87

or,

	Per cent.
Copper silicide : Cu_2Si	1.48
Other copper	34.13
Iron silicide	0.12
Free iron	0.17
Zinc	61.23
Free silicon	2.87

Experiment VI.

1 part silicide, 2 parts zinc.

	Per cent.
Cu	32.83
Fe	0.25
Zn	63.95
Si	2.97
Free Si	2.79

or,

	Per cent.
Copper silicide : Cu_2Si	0.82
Other copper	32.16
Iron silicide	0.11
Free iron	0.17
Zinc	63.97
Free silicon	2.79

When the percentage of zinc increases the percentage of copper silicide decreases of course. But it can also be seen from these figures that the copper silicide decreases much more rapidly than the copper. This is due to the more thorough decomposition of the copper silicide as the amount of zinc increases. This is especially evident in the following table:

		Ratio of copper to zinc.	Per cent. of the silicon in a free condition.[1]
Original silicide		100 : 0	trace
Experiment	I	100 : 27.6	trace
"	II	100 : 51.2	16.4
"	III	100 : 102.9	45.2
"	IV	100 : 147.8	87.5
"	V	100 : 173.3	91.4
"	VI	100 : 194.8	94.9

When the ratio of copper to zinc is 100 : 195, 94.9 per cent. of the silicon is in the free condition. The quantity of silicon then becomes so small that the difference between the amount of total and of free silicon comes within the limits of analytical errors.

Another obvious point is, that the addition of ¼ part of zinc does not liberate any silicon, while the addition of ½ part liberates a considerable amount. I have repeated experiments I. and II., with the same result, so that there can be no doubt as regards this point. It can readily be explained by assuming that in experiment I. the zinc found sufficient free copper to satisfy its affinity and that in experiment II. it did not. The zinc then left the copper silicide alone in experiment I., but in II. a contest has started between the zinc and silicon for the possession of the copper. If this be true, we can conclude that the composition of that compound of copper and zinc, which contains the highest amount of copper, is within the limits of

20.04 parts Zn : 40.97 parts Cu = 32.8 per cent. Zn and 67.2 per cent. Cu,

and

31.73 parts Zn : 39.40 parts Cu = 44.6 per cent. Zn and 55.4 per cent. Cu.

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[1] I have in each case deducted from the total amount of silicon that which is united to iron and I give the free silicon in per cents. of this deducted amount.

Judging from the large amount of free silicon in experiment II. we should expect the composition of this compound to be rather near the highest limit for copper. Such a compound might have the composition $ZnCu_2$, which contains 32.6 per cent. copper and 67.4 per cent. zinc. Charpy concluded from his experiments on the compounds in brass that the compound containing most copper has the composition $ZnCu_2$.

If we use a copper silicide containing less free copper we should expect that more silicon is liberated by the same amount of zinc, because the zinc and the silicon will sooner meet each other in a contest for the copper. The results have confirmed this belief.

I used a silicide which contains :

Silicide No. 2.

	Per cent.
Cu	81.14
Fe	2.52
Si	16.34
Free Si	4.37

or,

	Per cent.
Copper silicide : Cu_2Si	51.8
Free copper	38.8
Iron silicide	5.0
Free silicon	4.4

There is 4.37 per cent. free silicon in the sample, and I have therefore assumed the iron to be saturated with silicon. Supposing the iron to have been only half saturated with silicon, the results are still striking, as the figures given further below show.

To silicide No. 2 was added ½ part of zinc. The product contains :

Experiment VII.

1 part silicide, ½ part Zn.

	Per cent.
Cu	54.51
Fe	1.68
Zn	32.71
Si	11.10
Free Si	6.77

or,

	Per cent.
Copper silicide : Cu_2Si	14.2
Other copper	42.9
Iron silicide	3.4
Zinc	32.7
Free silicon	6.8

From these results the following table is prepared. If we compare it with experiments II. and III., we see that the same amount of zinc has liberated more silicon from silicide No. 2 than from silicide No. 1:

	Ratio of copper to zinc.	Per cent. of silicon in free condition. Supposing all iron is saturated with silicon.	Supposing the iron is half saturated with silicon.
Silicide No. 2	100 : 0	31.6	29.0
Experiment VII	100 : 60	71.9	66.0
Silicon liberated by zinc		40.3	37.0

The amount of silicon which has been liberated by 60 parts of zinc is here 37–40.3 per cent., while 51.2 parts of zinc in experiment II. liberate only 16.4 per cent. of silicon from silicide No. 1, and 102.9 parts of zinc in experiment III. liberate 45.2 per cent., which is just a little more than 60 parts liberate from silicide No. 2.

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Contributions from the Chemical Laboratory of Harvard College.

CVII.—ON THE COLORED COMPOUNDS OBTAINED FROM SODIC ALCOHOLATES AND PICRYL CHLORIDE.[1]

BY C. LORING JACKSON AND W. F. BOOS.

The work described in this paper is the continuation of a research begun by M. H. Ittner and one of us,[2] about three years ago, upon the colored products of the action of sodic alcoholates on certain aromatic nitro compounds. For a statement of the work of Lobry de Bruyn and Van Leent, and of Victor Meyer, on this subject, the reader is referred to that paper. The first object to which we turned our attention was the isolation and analysis of more substances of this class, since only three analyses of these bodies have been published. These three analyses led to the following formulas:

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[1] Presented to the American Academy of Arts and Sciences, January 12, 1898.

[2] This JOURNAL, **19**, 199.

$C_6H_3(NO_2)_3KOCH_3\frac{1}{2}H_2O$;[1]
$[C_6H_2(NO_2)_3COOKKOCH_3]_2CH_3OH$;[2]
and $C_6H_2OCH_3(NO_2)_2COONaNaOC_2H_5$.[3]

As dinitranisic acid had given Ittner and one of us[3] a comparatively stable compound, when treated with sodic ethylate, we at first tried to prepare similar compounds from it and other sodic alkylates; but a few experiments convinced us that the products from these reactions were too unstable for our purpose. Our attention was then called by one of our associates in this laboratory to the red substance formed by the action of sodic methylate on picryl chloride, and this has led to the discovery and analysis of the following compounds:

$C_6H_2(NO_2)_3OCH_3NaOCH_3$,
$C_6H_2(NO_2)_3OC_2H_5NaOC_2H_5$,
$C_6H_2(NO_2)_3OC_3H_7NaOC_3H_7$,
$C_6H_2(NO_2)_3OC_5H_{11}NaOC_5H_{11}$,
$C_6H_2(NO_2)_3OCH_2C_6H_5NaOCH_2C_6H_5$;

to which should be added a substance formed by the action of aqueous baric hydrate on a solution of trinitranisol in methyl alcohol, probably

$$[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2,$$

which was also obtained crystallized with 10 molecules of water. All of these substances have vivid red colors, and are decomposed by an acid, or more slowly by water, giving the picric ether. They are remarkably stable for compounds of this class.

The study of these substances has thrown some light on their constitution. The only published theory about bodies of this class is the suggestion made by the lamented Victor Meyer in his first paper[4] on this subject, that they might be formed by the replacement of one of the atoms of hydrogen on the benzol ring by potassium or sodium. According to this view our methyl compound would be formulated as follows: $C_6HNa(NO_2)_3OCH_3CH_3OH$; that is, it would contain a molecule of methyl alcohol of crystallization. Lobry de Bruyn[1] has brought forward an almost, if not absolutely, conclusive argument against this theory in his observation that sodium does not act on trinitrobenzol, even when in a boiling xylol solution, and therefore that trinitrobenzol cannot contain an atom of hydrogen which can be replaced by sodium. Our work described in this paper furnishes two arguments which confirm that of Lobry de Bruyn. First, it has shown that all of the substances analyzed so far contain, according to this theory, one molecule of alcohol of .crystallization, while the salt without alcohol of crystallization predicted by it ($C_6HNa(NO_2)_3OCH_3$, for instance) has never been obtained. Second, we have found that the methyl compound $C_6H_2(NO_2)_3OCH_3NaOCH_3$ can be heated to 130° without loss of weight, which could not have been the case had it contained methyl alcohol of crystallization, as is required by this theory. While neither of these arguments is so convincing as that derived by Lobry de Bruyn from the action of metallic sodium, they give it strong confirmation,[2] and we are satisfied therefore that Victor Meyer's theory in regard to these bodies should be abandoned, and that they should be considered as formed by the addition of the sodic alcoholate to the aromatic nitro compound. Whether the alcoholate is added to the carbon of the benzol ring or to the nitro group cannot be determined with our present knowledge, but possibly a way has been opened to decide this question by the discovery of the addition compounds formed from quinone and potassic ethylate or hydrate described by Astre,[3] $C_6H_4O_2KOC_2H_5$ and $C_6H_4O_2KOH$, and that from chloranil and sodic methylate, $C_6Cl_4O_2NaOCH_3$, obtained by H. A. Torrey and one of us.[4] These substances, by their striking colors, their formulas, mode of formation, and slight stability, seem to be related to the class of compounds discussed in this paper, and, if this connection can be proved, would show that the alcoholate is added to carbon and not to the nitro group. In continuing work in this direction an attempt will be made to find such substances not derived from quinones, as in quinones a special method of attachment of sodic alcoholate is possible, forming the hemiacetals. This line of work will be pursued in this laboratory during the coming year. It is worth mentioning that Astre independently of Victor Meyer explained the constitution of his compounds by supposing that the hydrogen on the quinone ring had been replaced by potassium, thus $C_6H_3KO_2C_2H_5OH$, a hypothesis which is inadmissible, as our derivative from chloranil undoubtedly belongs to the same class, and here ($C_6Cl_4O_2NaOCH_3$) no such arrangement of the atoms is possible. The details of this argument will be found in the paper by H. A. Torrey and one of us, already mentioned.

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[1] Lobry de Bruyn and Van Leent: Rec. Trav. Chim. Pays-Bas., **14**, 150.
[2] Van Leent: *Ibid*, **15**, 89.
[3] Jackson and Ittner: This JOURNAL, **19**, 210.
[4] Ber. d. chem. Ges., **27**, 3153.

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[1] Rec. Trav. Chim. Pays-Bas., **14**, 89.

[2] Ittner and one of us (This JOURNAL, **19**, 212) observed that the compound $C_6H_2(NO_2)_2OCH_3COONaNaOC_2H_5$ gave off alcohol when heated, but this observation is of little weight in favor of the theory, since the substance at the same time underwent a far-reaching decomposition, of which the alcohol may have been a product, instead of being alcohol of crystallization.

[3] Compt. rend., **121**, 530 (1895).

[4] This JOURNAL, **20**, 426.

By the decomposition of the corresponding colored compounds with an acid the following new picric ethers were obtained:

$C_6H_2(NO_2)_3OC_3H_7$, melting-point 43°;
$C_6H_2(NO_2)_3OC_5H_{11}$, melting at 68°–69°;

this was made from ordinary isoamyl alcohol; and

$C_6H_2(NO_2)_3OCH_2C_6H_5$, melting at 115°.

EXPERIMENTAL PART.

Action of Sodic Methylate on Picryl Chloride.

When a concentrated solution of picryl chloride in methyl alcohol was mixed with an excess of sodic methylate also dissolved in methyl alcohol, a mass of beautiful scarlet needles was formed immediately; or, if the solution was dilute, these scarlet needles appeared only upon standing. We first prepared the substance for analysis only by washing with water, in which it is but slightly soluble, and drying on a porous plate. The analysis of this preparation is numbered I. A second portion, after being washed with water, was recrystallized from methyl alcohol, which partially decomposed it, as white plates of trinitranisol could be distinguished mixed with the scarlet prisms of the new body. This impurity was removed by washing with benzol, in which the scarlet compound is nearly insoluble, but the trinitranisol very soluble. This preparation dried *in vacuo* was analyzed with the result numbered II.

The scarlet compound formed according to Clemm,[1] when a solution of picryl chloride in methyl alcohol was treated with sodic hydrate, was also prepared, and gave, on analysis, the result numbered III., which proves that it is identical with the product obtained by the action of sodic methylate.

I. 0.5280 gram of the substance gave, after decomposition with sulphuric acid, 0.1168 gram of sodic sulphate.

II. 0.3518 gram of the substance gave 0.0857 gram of sodic sulphate.

III. 0.1618 gram of the substance gave 0.0410 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OCH_3NaOCH_3$.	Found. I.	II.	III.
Sodium	7.69	7.17	7.89	7.90

The formula $C_6HNa(NO_2)_3OCH_3$ requires 8.68 per cent. of sodium.

These results indicate that the substance is formed by the addition of 1 molecule of sodic methylate to 1 molecule of trinitranisol. The sodic chloride, which must have been the other product of the reaction, was removed by washing with water in the preparation of the substance.

As, according to the theory proposed by Victor Meyer, this substance must contain a molecule of methyl alcohol of crystallization,

$$(C_6HNa(NO_2)_3OCH_3CH_3OH),$$

we next studied the effect of heat upon it. A sample dried for twenty-four hours *in vacuo* was heated to 100°–110°. After one hour's heating it had lost 0.0002 gram, and upon further heating remained constant. The heat was then increased to 130°–140°, but even at this temperature there was no loss in weight. In view of this experiment it seems impossible to maintain that the substance contains methyl alcohol of crystallization. When the temperature was raised to 165°, the substance decomposed, as was shown by a change in color.

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[1] J. prakt. Chem. [2], 1, 156.

Properties of the Addition-product of Trinitranisol and Sodic Methylate.—It crystallizes from methyl alcohol (with slight decomposition) in prisms apparently belonging to the monoclinic system, of a beautiful scarlet, or perhaps, rather vermilion, color with a bronze reflex. It decomposes at about 165°, and, if heated in the free flame, explodes with great violence. In the dry state it is comparatively stable, keeping well even when exposed to the air; but in contact with water it is gradually decomposed, forming trinitranisol, which, if the action is very long continued, passes into picric acid. Methyl alcohol dissolves it, but not without decomposition, as some trinitranisol is found mixed with the crystals obtained from such a solution; it is almost insoluble in benzol. Acids decompose it at once, forming a body, which after recrystallization from alcohol, melted at 64° and was therefore evidently trinitranisol; methyl alcohol was also set free, as shown by the odor.

Action of Ethyl Alcohol on the Addition-product of Trinitranisol and Sodic Methylate.

This work was undertaken in the hope of deciding whether the addition-product contained methyl alcohol of crystallization, as in that case the methyl alcohol must be replaced by ethyl alcohol upon recrystallization from this solvent, whereas, if the second methyl group was not present in alcohol of crystallization, it might either remain in the compound under these conditions, or be replaced by the ethyl group. If, therefore, the methyl compound were unaltered by crystallization from ethyl alcohol, it could not contain methyl alcohol of crystallization. Unfortunately, the experiment showed that the methyl group was replaced by ethyl, and therefore no inference in regard to the constitution of the body could be drawn from this work.

On recrystallizing the methyl compound from ethyl alcohol a substance was obtained closely resembling the original methyl compound in color, crystalline form, and properties, but which gave the following result on analysis after having been dried *in vacuo*:

0.3012 gram of the substance gave 0.0681 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_2H_5NaOC_2H_5$.	Found.
Sodium	7.23	7.32

This result seems to indicate that the body is the ethyl compound, but is not conclusive, as the difference between the percentages of sodium in the methyl and ethyl compounds is only 0.46 per cent., and the experimental error may well reach or even exceed this amount in the case of compounds which are so hard to purify on account of their instability. But we do not have to depend on the analysis in this case, as upon decomposing the substance with an acid, and recrystallizing the product from alcohol, long, nearly colorless needles were obtained, which melted at 78°–79°, and were, therefore, the ethyl ether of picric acid. We hope that further experiments in this direction will be tried in this laboratory during the coming year.

An attempt to make this ethyl compound direct from sodic ethylate and picryl chloride did not lead to the desired result; a mass of red crystals was formed, to be sure, but these dissolved, when treated with water, to wash out the sodic chloride, giving a red solution, which gradually turned yellow, and then deposited needles of ethyl picrate.

Action of Sodic Propylate on Picryl Chloride.

A concentrated solution of picryl chloride in benzol was mixed with an excess of sodic propylate dissolved in a little propyl alcohol; a heavy precipitate of red needles was formed, which was washed thoroughly at first with benzol and afterward with water. It was then dried on a porous plate, and at last at 110°, when the following results were obtained on analysis:

I. 0.2960 gram of the substance gave, on combustion,[1] 0.4390 gram of carbonic dioxide and 0.1260 gram of water.

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[1] The substance was mixed with chromic oxide to decompose the sodic carbonate formed.

II. 0.6223 gram of the substance gave 0.1235 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_3H_7NaOC_3H_7$.	Found.	
		I.	II.
Carbon	40.79	40.45	....
Hydrogen	4.53	4.73	....
Sodium	6.54	....	6.44

The formula $C_6HNa(NO_2)_3OC_3H_7$ requires 36.85 per cent. of carbon, 2.73 of hydrogen, and 7.85 of sodium.

Properties of the Addition-product of Propyl Picrate and Sodic Propylate.—It resembles the methyl compound closely, but its color is a somewhat lighter red, and it is not quite so stable when exposed to the air. Acids decompose it giving propyl alcohol, recognized by the smell, and the propyl picrate, which has not been described heretofore. Propyl picrate crystallizes in fine, nearly colorless needles, melting at 43°, and is easily soluble in all the common solvents. If allowed to stand with water or an acid, it is decomposed with the formation of picric acid.

Action of Sodic Isoamylate on Picryl Chloride.

A benzol solution of picryl chloride was mixed with an excess of sodic isoamylate dissolved in a little isoamyl alcohol, and the amorphous orange precipitate formed was washed thoroughly with benzol and afterward with water, and dried at first on a porous plate finally at 110°, when it gave the following results on analysis :

0.2894 gram of the substance gave 0.0490 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OCH_5H_{11}NaOC_5H_{11}$.	Found.
Sodium	5.62	5.48

The formula $C_6HNa(NO_2)_3OC_5H_{11}$ requires 7.16 per cent. of sodium.

Properties of the Addition-product from Isoamyl Picrate and Sodic Isoamylate.—This substance forms an orange amorphous mass, which is decomposed by all the liquids which dissolve it, so that we could not try to crystallize it. It is essentially insoluble in water or benzol. Acids decompose it, setting free isoamyl alcohol, recognized by its smell, and isoamyl picrate.

Isoamyl Picrate, $C_6H_2(NO_2)_3OC_5H_{11}$.

This substance was obtained by the action of an acid on the addition-product just described. It was purified by crystallization from alcohol, until it showed the constant melting-point 68°–69°, when it was dried *in vacuo*, and analyzed with the following result:

0.1311 gram of the substance gave, on combustion, 0.2117 gram of carbonic dioxide and 0.0558 gram of water.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}$.	Found.
Carbon	44.14	44.02
Hydrogen	4.34	4.73

Isoamyl picrate crystallizes from alcohol in nearly colorless hexagonal plates, which melt at 68°–69°. It is decomposed by standing with water or acids, but in this respect is much more stable than propyl picrate.

Action of Sodic Benzylate on Picryl Chloride.

When picryl chloride in benzol solution was treated with an excess of sodic benzylate, a mass of beautiful red needles was formed, which, after washing thoroughly with benzol and water, was dried on a porous plate, and afterward at 110°, and analyzed with the following result:

0.3125 gram of the substance gave 0.0470 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_7H_7NaOC_7H_7$.	Found.
Sodium	5.12	4.87

The formula $C_6HNa(NO_2)_3OC_7H_7$ requires 6.74 per cent. of sodium.

Properties of the Addition-product of Benzyl Picrate and Sodic Benzylate.—This substance crystallizes in red needles of a somewhat lighter shade than the propyl compound, and shows a distinct fluorescence. It is also more stable than the propyl compound, since a sample of it stood exposed to the air in a watch-glass for some months without any visible change. Water decomposes it, but much more slowly than the other compounds of this class. In this decomposition, as well as in that by an acid, the principal products are benzyl alcohol and benzyl picrate.

Benzyl Picrate, $C_6H_2(NO_2)_3OC_7H_7$.

This substance, prepared by the action of an acid on the addition-product just described, was purified by recrystallization from alcohol, until it showed the constant melting-point 115°, when an analysis gave the following result:

0.3828 gram of the substance gave, on combustion, 0.6805 gram of carbonic dioxide and 0.1090 gram of water.

	Calculated for $C_6H_2(NO_2)_3OC_7H_7$.	Found.
Carbon	48.90	48.48
Hydrogen	2.82	3.16

Benzyl picrate crystallizes from alcohol, in which it is difficultly soluble, in nearly colorless plates, melting at 115°. It is gradually decomposed by acids, forming picric acid.

Action of Baric Hydrate on Picryl Chloride, or on Trinitranisol in Methyl Alcoholic Solution.

When a concentrated solution of picryl chloride in methyl alcohol was treated with an excess of an aqueous solution of baric hydrate, a dense mass of red crystals was formed, which were collected, and washed with water as quickly as possible to prevent the formation and precipitation of baric carbonate from the excess of baric hydrate. The crystals were then dried on a porous plate. Trinitranisol dissolved in methyl alcohol gives the same compound, when treated with aqueous baric hydrate, and as thus a purer product was obtained, we prepared most of our material in that way. Analysis of the air-dried substance gave the following result:

0.8154 gram of substance gave 0.2394 gram of baric sulphate.

	Calculated for $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2.10H_2O$.	Found.
Barium	16.37	17.26

As this indicated that the substance contained water of crystallization, its behavior when heated was studied.

I. 0.7733 gram of the air-dried substance lost 0.1622 gram at 110°–130°.

II. 0.3513 gram of the air-dried substance lost 0.0736 gram at 110°–130°.

III. 0.8206 gram of the air-dried substance lost 0.1738 gram at 110°–130°.

	Calculated for	Found.		
	$[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2.10H_2O$.	I.	II.	III.
Water	21.50	20.97	20.95	21.17

I. 0.4064 gram of the substance dried at 110°–130° gave 0.1504 gram of baric sulphate.

II. 0.4616 gram of the substance gave 0.1694 gram of baric sulphate.

III. 0.1296 gram of the substance gave, on combustion, 0.1201 gram of carbonic dioxide[1] and 0.0259 gram of water.

IV. 0.2654 gram of the substance gave[2] 31.4 cc. of nitrogen under a pressure of 753.1 mm. and at a temperature of 20°.5.

	Calculated for		Found.			
	$[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2$.	$[C_6H(NO_2)_3OCH_3]_2Ba$.	I.	II.	III.	IV.
Ba	20.85	22.05	21.76	21.58	....	....
C	25.56	27.05	....	....	25.26	....
H	1.83	1.29	....	....	2.22	....
N	12.78	13.53	....	....	....	13.40

These results, therefore, do not decide with certainty between the two formulas, for, although the percentage of carbon speaks strongly in favor of $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2$, the determinations of barium agree with the percentage calculated for the second formula. As the most probable impurity in the substance was baric carbonate, we shall provisionally adopt the formula containing baric hydrate.

Properties of the Addition-product of Trinitranisol and Baric Hydrate.—It forms needles of a fine red color verging toward scarlet. When heated to 110°, it loses its water of crystallization, and turns a beautiful dark crimson, but the dried salt absorbs water very eagerly from the air, regaining its scarlet-red color. This fact necessitates great care in handling the dried salt during the process of analysis. Part, but not all, of the water of crystallization is given off *in vacuo*. It is insoluble in water. Acids decompose it, giving trinitranisol, but no alcoholic odor was observed.

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[1] Chromic oxide was used to decompose the baric carbonate formed. The substance was spread out in a long copper boat, and heated very carefully to avoid explosions.

[2] The substance was mixed with sand to decompose any baric nitrite which might have been found.

Calcic hydrate added to a solution of picryl chloride in methyl alcohol gave a red precipitate, but this decomposed almost immediately with formation of trinitranisol. Dinitranisic acid dissolved in methyl alcohol gave a magnificent purple coloration, when treated with aqueous baric hydrate, but the substance formed was very unstable. It is mentioned here, as it forms an additional argument for classing the trinitranisol compounds described in this paper with the colored derivatives of dinitranisic acid discovered by Ittner and one of us.

The work will be continued in this laboratory.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

XIV.—ON THE ACTION OF ORTHODIAZOBENZENESULPHONIC ACID ON METHYL AND ETHYL ALCOHOL.[1]

BY E. C. FRANKLIN.

Preparation of Ortho- and Metamidobenzenesulphonic Acid.

As the two acids were obtained in considerable quantity and by a method somewhat different from that employed by Limpricht[2] and that employed by Shober and Kiefer,[3] an account of the method is here given.

Preparation of the Nitrosulphonic Acids.—250 grams of pure benzene and 300 cc. of fuming sulphuric acid were introduced into a flask of 1 liter capacity provided with a cork into which is fitted a long glass tube to serve as a reflux condenser. The reaction began at once, accompanied by considerable evolution of heat. The action was assisted by shaking, care being taken not to allow it to proceed so rapidly as to raise the temperature of the mixture to the boiling-point of benzene. At the expiration of about an hour the benzene had almost completely passed into solution. A small quantity which persistently resisted the action of the acid was removed by transferring the acid mixture to a flask of such size that the acid mixture filled it well up into the neck. After standing a short time the benzene collected in the neck of the flask and was removed by means of a pipette. The solution of benzenesulphonic acid was then returned to the larger flask and treated with fuming nitric acid of specific gravity of 1.50. The nitric acid was added very cautiously. At the beginning of the operation the reaction was so violent that it was necessary to suspend the operation from time to time, and cool the mixture by immersion in cold water. Towards the end of the operation the action became much less violent, and finally when the addition of a considerable quantity of acid produced no further elevation of temperature the nitration was considered finished. The acid mixture was then poured into a large quantity of water and allowed to stand until a small quantity of dinitrobenzene which had been formed, had subsided. The clear yellow liquid was then decanted and neutralized with chalk. The solution was filtered from gypsum and excess of chalk, and the calcium salts converted into the potassium salts by the addition of potassium carbonate. On filtering off the calcium carbonate, a bright yellow solution of the potassium salts was obtained. The nitro acids might at this stage have been reduced to the amido acids and these subsequently separated, but after several attempts at this method, it was found advisable first to separate the nitro acids from the solution and then effect their reduction in solutions free from nitric acid. If the reduction is effected in the solution containing nitrates, a black solution results, from which the amido acids can be but very imperfectly separated. The solution of the potassium salts was concentrated and set aside to crystallize. The first crops were almost pure potassium metanitrobenzenesulphonate. They were reserved and reduced separately, furnishing pure metamidobenzenesulphonic acid, while the latter crystallizations, which were mixtures of all three modifications, were reduced without separation from each other, furnishing a mixture of the three amidobenzenesulphonic acids.

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[1] From the Author's Dissertation, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1894. The investigation included the meta acid as well as the ortho, but as Dr. Shober has communicated the results reached by him in the investigation of the meta acid, and these results are practically the same as those reached by the Author, no account of this part of the investigation is here given.

[2] Ann. Chem. (Liebig), **177**, 61.

[3] This JOURNAL, **17**, 454.

Reduction of Metanitrobenzenesulphonic Acid.—The reduction can be readily effected, either by the use of tin and hydrochloric acid or by ammonium sulphide. Limpricht used ammonium sulphide, which has also in this investigation been found preferable to tin and hydrochloric acid.

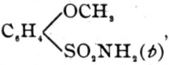
The potassium salt was dissolved in water by the aid of heat, and the solution made strongly alkaline by the addition of ammonium hydroxide. Into the solution thus prepared hydrogen sulphide was conducted until complete saturation had taken place. The solution was then heated on a water-bath until the excess of ammonium sulphide was completely expelled. Hydrochloric acid was then added, the solution filtered from separated sulphur, and set aside to crystallize. After standing over night the acid separated. By re-solution of the crude acid in boiling water and treatment with bone-black, a colorless solution was obtained, which, when allowed to stand, furnished the crystallized acid in pure condition.

Metamidobenzenesulphonic acid was thus obtained in the form of slender, colorless needles without water of crystallization. It is difficultly soluble in cold water, more readily in hot. It becomes discolored by exposure, and decomposes without melting upon being heated.

Reduction of the Mixture of the Ortho-, Meta-, and Paranitrobenzenesulphonic Acids, and the Separation and Purification of the Orthoamido Acid.—The mixture of the potassium salts of the three isomeric acids, obtained as described above, was treated with ammonium hydroxide and hydrogen sulphide. The acid solution, after separation of the sulphur, was boiled with bone-black and set aside to crystallize. By proper regulation of the concentration of the solution the three amido acids crystallized out, each in its characteristic form. The meta modification was deposited as slender needles; the ortho in large, transparent, rhombohedrons which were anhydrous, while the para acid formed thick, leaf-like crystals with water of crystallization. From the crystalline mixture thus obtained, the light, slender crystals of the meta acid were removed, by washing, from the larger and heavier crystals of the isomeric acids. The remaining mixture of the ortho and para acids was then partially dried by pressure between folds of absorbent paper, and the desiccation completed in the air-bath at a temperature of 110°–120°, by which treatment the para acid lost its water of crystallization and crumbled to powder. The anhydrous ortho acid was not affected, and was separated from the pulverulent para acid by means of a sieve. The ortho acid was then, after several recrystallizations from hot water and treatment with bone-black, obtained in pure condition.

In one experiment a yield of over four per cent. was obtained. Other experiments were less satisfactory.

Orthoamidobenzenesulphonic acid was thus obtained in fine crystals of a rhombohedral habit, and usually of a pronounced pink color. It is difficultly soluble in cold water, more readily in hot water, and decomposes without melting on being heated.

The paramidobenzenesulphonic acid from the above mixture was purified by recrystallization, and its identity with sulphanilic acid, prepared by the action of sulphuric acid on aniline, was confirmed. A small quantity of the acid was diazotized, the diazo compound decomposed with methyl alcohol, and the resulting methoxybenzenesulphonic acid converted into the amide. This amide,[1]  $C_6H_4\begin{cases}OCH_3\\SO_2NH_2(p)\end{cases}$, crystallized in colorless, well-formed needles melting at 112°.

Preparation of Orthodiazobenzenesulphonic Acid.

An excellent yield of the diazo compound was obtained by suspending the amido acid in ordinary alcohol and passing a stream of nitrous fumes into the mixture. The reaction takes place with remarkable ease.

Ten grams of the finely powdered amido acid were suspended in 25 cc. ordinary alcohol and a rapid stream of nitrous fumes passed into the mixture. The contents of the flask became warm, but the temperature was not allowed to rise above 40°–50°. In about ten minutes the reaction was complete. An equal volume of ether was then added to the mixture, and the flask with its contents left at rest in a freezing-mixture of ice and salt for several hours. The diazo compound was then filtered off, washed with ether, and spread out on filter-paper to dry. A yield of 10 grams was obtained. Orthodiazobenzenesulphonic acid thus prepared is a beautiful, white, crystalline powder, which slowly becomes colored on exposure. It is comparatively stable and if protected from air and moisture it can be kept for a considerable time without suffering appreciable change. It explodes by contact with flame or by percussion.

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[1] Shober : This Journal, 15, 380.

The Relative Susceptibility of the Ortho-, Meta-, and Paramidobenzenesulphonic Acids to the Action of Nitrous Acid.

It is interesting to compare, in passing, the relative susceptibilities of the three isomeric amidobenzenesulphonic acids to the action of nitrous acid. Metamidobenzenesulphonic acid cannot be satisfactorily diazotized by treatment in suspension in alcohol with nitrous fumes, as the author has found by repeated trials. Suspended in water, however, it is diazotized without the least difficulty. The paramidobenzenesulphonic acid must, according to Shober,[1] be very finely powdered. When this preliminary has been properly attended to, a quantity of the acid suspended in alcohol can be diazotized in from one to two hours. It has been determined in the present investigation that the para acid is diazotized with much more difficulty under the above conditions than is the ortho acid. Mr. Daniel Base, working in this laboratory, found it quite impossible to effect complete transformation of sulphanilic acid by this method. There always remained behind, when the diazo acid was decomposed, a residue of sulphanilic acid. The remarkable ease with which the ortho acid can be diazotized under these conditions is evident from the description of its preparation above. Similar relations between the paratoluidineorthosulphonic acid and the paratoluidinemetasulphonic acid have been pointed out by Metcalf.[2] The latter compound in which the amido and sulphonic acid groups occupy the ortho position relatively to each other, is readily diazotized by suspension in alcohol, while the former acid, in which these two groups occupy the meta position relatively to each other, cannot satisfactorily be so diazotized. It is, of course, recognized that difference of solubility of the amido compounds may account for their observed behavior when suspended in alcohol.

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[1] Dissertation, 1892, p. 7.

[2] This JOURNAL, **15**, 305.

Decomposition of Orthodiazobenzenesulphonic Acid with Methyl Alcohol.

1. *At Atmospheric Pressure.*—Three grams of the diazo compound and 25 cc. methyl alcohol were heated in a flask with reflux-condenser. The reaction was complete in twenty minutes, yielding a clear and but slightly colored solution. The decomposition-products were treated in the usual manner for the amides. 0.8 gram of pure methoxybenzenesulphonamide, melting at 171°, was obtained, while no benzenesulphonamide could be found. The amides in every case of decomposition of the ortho acid were found to be less contaminated with the gummy impurities than were the decomposition-products of the meta acid.

2. *At Atmospheric Pressure + 850 mm. of Mercury.*—Three grams of the diazo compound, together with 100 cc. methyl alcohol, were introduced into the pressure-flask[1] and the decomposition carried out at the above indicated pressure. The reaction was complete in five minutes, furnishing a clear and but slightly colored solution. The alcohol was removed by distillation, and the residue treated as usual for the amides. Only the methoxybenzenesulphonamide, melting at 171°, could be identified.

3. *At Atmospheric Pressure — 450 mm. of Mercury.*—Five grams of the diazo compound, together with 60 cc. methyl alcohol, were introduced into the flask of the apparatus for decomposition at diminished pressure,[2] and after adjustment of the pressure, the contents of the flask were heated to boiling. The solution slowly took on a light-red color, and after about seven hours' boiling the decomposition was complete. The alcohol was removed by distillation, and the residue treated as in the foregoing experiments for the amides. 1.54 grams of methoxybenzenesulphonamide, melting at 171°, was ob-

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[1] Remsen and Palmer: This JOURNAL, **8**, 245.

[2] Parks: This JOURNAL, **15**, 324.

tained, while from the mother-liquors no benzenesulphonamide could be separated.

Orthomethoxybenzenesulphonamide crystallizes in colorless needles which are but sparingly soluble in cold water, more readily soluble in hot water or in alcohol.

A determination of sulphur in the amide obtained in these experiments resulted as follows: 0.2242 gram of the substance gave 0.2777 gram barium sulphate, which corresponds to 17.04 per cent. sulphur. The percentage of sulphur calculated for $C_6H_4(OCH_3)(SO_2NH_2)$ is 17.11.

Further proof of the identity of this compound was furnished by chlorine and sulphur determinations in the orthomethoxybenzenesulphone chloride, which compound has also been prepared by Haitinger.[1]

Preparation of Orthomethoxybenzenesulphone Chloride.—Fifteen grams of orthodiazobenzenesulphonic acid were decomposed with 125 cc. methyl alcohol at a pressure of 850 mm. above atmospheric pressure. The reaction was complete in forty-five minutes, furnishing as a product a clear and but slightly colored solution. The acid liquid was neutralized with pure barium carbonate and the attempt made to obtain a pure barium salt. A quantity of crystals were obtained which were in all probability the impure barium salt. This was not further studied, as it seemed more desirable to use the material for the preparation of the chloride. The barium salt was changed into the potassium salt, and this, by the usual method with phosphorus pentachloride, was converted into the acid chloride. As noticed when working with smaller quantities in the experiments above, this chloride separated from the reaction-mixture, on treatment with water, as a waxy solid. It was washed with water and dissolved in ether. The ethereal solution was dried with calcium chloride, filtered, and placed in a desiccator to crystallize. From the concentrated solution the chloride separated in nearly colorless plates, which upon recrystallization from petroleum ether (b. p. below 100°) was deposited as stout needles. It was found to melt at 56°. Haitinger[2] prepared this chloride from orthophenolsulphonic acid and found its melting-point to be 55°.

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[1] Monatsch., 4, 173.

[2] *Loc. cit.*

Determinations of chlorine and sulphur in this compound gave the following results:

I. 0.2266 gram of the substance gave 0.1585 gram silver chloride, which corresponds to 17.29 per cent. chlorine. The percentage of chlorine calculated for $C_6H_4(OCH_3)(SO_2Cl)$ is 17.19.

II. 0.2030 gram of the substance gave 0.2335 gram barium sulphate, which corresponds to 15.81 per cent. sulphur. The percentage of sulphur calculated for $C_6H_4(OCH_3)(SO_2Cl)$ is 15.50.

Decomposition of Orthodiazobenzenesulphonic Acid with Ethyl Alcohol.

1. *At Atmospheric Pressure.*—Five grams of the diazo compound and 75 cc. ethyl alcohol were decomposed as usual. In from five to seven minutes the decomposition was completed. The resulting light-red colored solution was treated in the usual manner for the amides. The only amide obtained was an ethoxybenzenesulphonamide, melting at 156°.

2. *At Atmospheric Pressure + 850 mm. of Mercury.*—Five grams of the diazo compound, together with 75 cc. ethyl alcohol, were introduced into the pressure-flask and the decomposition initiated under full pressure, but because of an accident it was completed at atmospheric pressure. 0.75 gram of the pure ethoxybenzenesulphonamide, melting at 156°, was obtained.

Whether or not the hydrogen reaction takes place in these decompositions could not be definitely determined from the above experiments. The melting-points of the two compounds, orthoethoxybenzenesulphonamide and benzenesulphonamide, lie so near together that determinations of these constants could not be made use of as guides. Repeated attempts to obtain crops of mixed crystals of different habit, from the mother-liquors, were unsuccessful. This, together with the fact that the amide obtained showed a constant melting-point, led to the conclusion that the hydrogen reaction did not take place.

A sulphur determination resulted as follows: 0.2203 gram of the substance gave 0.2547 gram barium sulphate, which corresponds to 15.89 per cent. sulphur. The calculated percentage of sulphur in $C_6H_4(OC_2H_5)(SO_2NH_2)$ is 15.92.

Orthoethoxybenzenesulphonamide crystallizes from hot dilute alcohol as colorless, slender needles. It is almost completely insoluble in cold water, and but sparingly soluble in hot water.

G. T. Moody[1] prepared the orthoethoxybenzenesulphonamide by the ethylation of parabromphenol, sulphonation of the bromphenetol thus formed, reduction of the bromphenetolorthosulphonic acid, and conversion of the resulting acid into its amide. He found its melting-point to be 156°.

Action of Fuming Nitric Acid on Alkoxybenzenesulphonamides.

1. *On Paramethoxybenzenesulphonamide.*—Shober[2] has shown that when paramethoxybenzenesulphonamide is treated with nitric acid metadinitrobenzene is formed. It was thought desirable to study this reaction somewhat further, and also to study the action of nitric acid on the ortho and meta amides. That metadinitrobenzene is not the only product of the action of nitric acid on this amide was suspected because of the small yield of the nitro product obtained. In order to determine what other compounds might be formed 4.4 grams paramethoxybenzenesulphonamide were added gradually to 10 grams of fuming nitric acid, of specific gravity 1.52, kept cold by a freezing-mixture of ice and salt. It was observed that when the temperature of the acid was kept well down the quantity of metanitrobenzene formed was always much decreased. The acid liquid was diluted with water, which caused a separation of a small quantity of dinitrobenzene. This was filtered off, and the filtrate evaporated with alcohol for the purpose of removing the excess of acid. The thick syrupy residue was diluted with water and neutralized with potassium hydroxide, when immediately a crop of crystals of the potassium salt of an acid of the composition given below was obtained:

The analysis of the compound yielded the following results:

I. 0.3498 gram gave 0.4021 gram carbon dioxide and 0.0751 gram water.

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[1] J. Chem. Soc., 1892–93, 214.

[2] This JOURNAL, 15, 390.

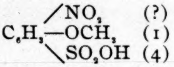
II. 0.2854 gram gave 13.9 cc. nitrogen measured over water at a temperature of 18°, and 726 mm. barometric pressure.

III. 0.1265 gram gave 0.1127 gram barium sulphate.

IV. 0.1448 gram gave 0.0467 gram potassium sulphate.

	Calculated for $C_7H_6O_6NSK$.	Found.			
		I.	II.	III.	IV.
C	31.00	31.34	....	....	....
H	2.21	2.38	....	....	....
N	5.17	....	5.31	....	....
S	11.81	....	....	12.23	....
K	14.38	....	....	....	14.46

The principal product of the action of nitric acid on paramethoxybenzenesulphonamide is hence a mononitroparamethoxybenzenesulphonic acid of the formula:



$$C_6H_3\begin{array}{l} \diagup NO_2 \quad (?) \\ -OCH_3 \quad (1) \\ \diagdown SO_2OH \quad (4) \end{array}$$

A portion of this acid was reduced to the amido compound, while another was converted into the sulphonamide by successive treatment with phosphorus pentachloride and ammonium hydroxide. The sulphonamide was obtained as well-formed, yellow needles melting at 138°–140°.

2. *On Metamethoxybenzenesulphonamide.*—Three grams of the amide were added gradually to 10 grams of fuming nitric acid. The experiment was carried out as nearly as possible in the same manner as described for the corresponding para compound. No dinitrobenzene was obtained.

A second experiment, in which 5 grams of the amide and 20 grams of the acid were used, also failed to give any dinitrobenzene. The solutions from these two experiments were united, and evaporated with alcohol to remove the excess of nitric acid. The residue was taken up with water and neutralized with barium carbonate. The filtered solution, after boiling with bone-black and concentration, deposited crystals of a barium salt of a nitrosulphonic acid. This salt deflagrated when heated on platinum foil, and a test for sulphur showed it to contain this element.

3. *On Orthomethoxybenzenesulphonamide.*—One gram of the

amide was added to 4 grams of fuming nitric acid as in the previous experiments. Upon dilution a small quantity of yellow needles of metadinitrobenzene, melting at 88°, crystallized out.

4. *On Paraethoxybenzenesulphonamide.*—Two and one-half grams of the amide, added as in the above experiments to 10 grams of fuming nitric acid, gave on dilution a considerable yield of dinitrobenzene. This substance, after being once recrystallized from dilute alcohol, melted at 83°–84°.

Table Showing the Results of the Decompositions of the Diazobenzenesulphonic Acids with

1. *Methyl Alcohol.*

	At atmospheric pressure — 450 mm. mercury	At atmospheric pressure.	At atmospheric pressure + 850 mm. mercury.
Ortho acid	Methoxy[3]	Methoxy	Methoxy
Meta acid[1]	Methoxy Hydrogen	Methoxy Hydrogen	Methoxy
Para acid[2]	Hydrogen	Hydrogen Methoxy	Methoxy Hydrogen

2. *Ethyl Alcohol.*

	At atmospheric pressure.	At atmospheric pressure + 850 mm. mercury.
Ortho acid	Ethoxy	Ethoxy
Meta acid[1]	Ethoxy Hydrogen	Ethoxy Hydrogen
Para acid[2]	Hydrogen	Hydrogen

Conclusion.

The more important results reached in this investigation may be summarized as follows:

1. When orthodiazobenzenesulphonic acid is decomposed with methyl alcohol the methoxy product only is obtained.
2. When the decomposition of orthodiazobenzenesulphonic acid is effected with ethyl alcohol the alkoxy reaction only takes place.
3. Higher pressures favor the alkoxy reaction.

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[1] Shober and Kiefer: This JOURNAL, **17**, 454.

[2] Shober: This JOURNAL, **15**, 379.

[3] Large type signifies large yield; small type signifies smaller yield.

4. The yield of the alkoxyamide is greater when the decomposition of the diazo compound is made with the simpler alcohol.

5. When paramethoxy- or paraethoxybenzenesulphonamide is treated with fuming nitric acid one of the products is metadinitrobenzene. At the same time a nitro substitution-product of paramethoxybenzenesulphonic acid is formed.

6. When metamethoxybenzenesulphonamide is treated with fuming nitric acid, no metadinitrobenzene is formed.

7. When orthomethoxybenzenesulphonamide is treated with fuming nitric acid one of the products formed is metadinitrobenzene.

ON THE TASTE AND AFFINITY OF ACIDS.

BY J. H. KASTLE.

Quite recently Richards[1] has shown that, qualitatively at least, a definite relation exists between the sour taste of acids and the extent of their dissociation, and he has succeeded in proving that the sense of taste might be employed in the laboratory with far greater precision than has hitherto been thought possible. In 1893, it also occurred to the writer that there might be some connection between the degree of sourness of acids and their chemical affinity, and accordingly an investigation of the subject was then undertaken in which the taste of nineteen acids was compared on sixteen different individuals. About 400 observations were made and recorded. Other matters became pressing, however, and the investigation was left in just the shape in which it is here presented, the idea being to take it up again when the opportunity offered. While this opportunity never presented itself it is believed that the results reached at that time are of sufficient interest, especially in the light of the recent developments of the subject, to warrant the following discussion. It should be observed in this connection that no claim of priority is made either directly or indirectly, and no interference with the work of others is intended. It is believed, however, that a good deal of evidence has been collected by the writer, independently, which has an important bearing on the question concerning the relation between the taste of acids and their strength, and in the following this is given simply for what it is worth.

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[1] This JOURNAL, 20, 121.

As the result of some preliminary work, it was found that a dilution of $\frac{1}{50}$ normal was likely to prove best suited for the purpose of comparison. Nineteen acids of this dilution were used in the investigation. These were as follows: Hydrochloric, nitric, hydrobromic, sulphuric, benzenesulphonic, iodic, propionic, monochloracetic, acetic, formic, glycolic, lactic, malonic, oxalic, citric, phthalic, malic, succinic, and tartaric. In order to do away, as largely as possible, with any individual idiosyncrasies relative to the sense of taste, it was thought advisable to make the comparisons on as large a number of individuals as practicable. Sixteen persons, besides the writer, kindly allowed the necessary tests to be made upon them. These were as follows: H. H. Hill, Clara Shaw, Anne May, Mary McCann, Irvine Lyle, R. L. Weaver, W. J. Calvert, A. M. Peter, M. A. Scovell, F. P. Anderson, Henry Curtis, H. Garman, Alice Shelby, H. S. Bush, C. W. McElroy, S. E. Bennett. I take this opportunity to thank them for their kindness in the matter.

In conducting the tests equal amounts of the two acids being compared, usually about 1 cc., were placed one after the other on the tongue of the observer, allowing sufficient time for the taste of the first acid to disappear before bringing the second one on the tongue. The person on whom the test was made was then asked to decide which acid was the sourer of the two. It occasionally happened, though not often, that the person would wish to taste the two acids several times in succession, and in different order, before venturing an opinion concerning their relative sourness.

In consequence of the voluminousness of the results it has not been thought advisable to give them all in detail; and in the following they are presented only in a general way.

Altogether 403 observations were made. A careful examination of these results shows that, leaving out of consideration 14 observations on the strongest acids, such as hydrochloric and nitric,[1] etc., there are 296 comparisons in which the stronger acid was found to have the sourer taste, and only 93 in which the weaker acid was said to taste sourer. In other words, 76.09 per cent. of the observations are in support of the conclusion that a definite relation exists between the sour taste of acids and their affinity, or, as Richards[2] has expressed it, between the sour taste and their electrolytic dissociation, whereas, 23.91 per cent. of the observations are opposed to this conclusion. It should be mentioned in this connection, however, that in 157 of these observations a very strong acid was compared with a very weak one. In 126 instances the very strong acid was found to taste sourer than the very weak, whereas in 31 instances the reverse of this was found to be true; *viz.*, the very weak acid tasted sourer than the very strong one. This gives a percentage of error of 19.74—a number which differs but little from that found for all the observations; *viz.*, 23.91, so that the general character of the results would seem to be the same whether the comparisons are made between acids differing but slightly in strength, or between those differing most widely in this respect.

In view of these results, therefore, it can scarcely be doubted that some fundamental and general relation exists between the taste of acids and their affinity. The results obtained with the several members of a series of related acids are especially interesting in this connection. In the case of formic, acetic, and propionic acids the following data have been compiled from the observations :

In 11 observations formic acid was found to be sourer than acetic.

In 18 observations formic acid was found to be sourer than propionic.

In 2 observations acetic acid was found to be sourer than formic.

In 9 observations acetic acid was found to be sourer than propionic.

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[1] These 14 observations on the strongest acid cannot be put in either of the two classes given in the above for the reason that all of these acids have the same strength. It matters really very little, however, whether these few observations are counted for or against the views discussed in the above.

[2] *Loc. cit.*

In 1 observation propionic acid was found to be sourer than formic acid.

In no observation was propionic acid found to be sourer than acetic.

So far, then, as the sourness is concerned, these 3 acids stand to one another in the relation formic > acetic > propionic; and, as is well known, these acids stand to one another in a similar relation as regards their chemical affinity. Similar results were obtained in the case of monochloracetic and acetic acids:

In 9 observations monochloracetic acid was found to be sourer than acetic.

In 2 observations acetic acid was found to be sourer than monochloracetic.

The coefficients of affinity of these two acids, as given by Ostwald, are for monochloracetic 0.049 and for acetic 0.00424.

So in the case of several of the common dibasic organic acids belonging to the same group we meet with differences in taste which correspond almost exactly to differences in affinity.

For example:

In 3 observations succinic acid was found to be sourer than malic.

In no observation was succinic acid found to be sourer than tartaric.

In 11 observations malic acid was found to be sourer than succinic.

In 1 observation malic acid was found to be sourer than tartaric.

In 3 observations tartaric acid was found to be sourer than succinic.

In 9 observations tartaric acid was found to be sourer than malic.

In order of taste these acids are, therefore, tartaric > malic > succinic. They are the same in order of affinity.

The following are the results obtained with glycolic and lactic acids as compared with one another and with acetic and propionic, respectively:

In 10 observations glycolic acid was found sourer than acetic.

In 6 observations glycolic acid was found sourer than propionic.

In 3 observations glycolic acid was found sourer than lactic.

In 5 observations acetic acid was found sourer than glycolic.

In no observation was acetic acid found sourer than lactic.

In 3 observations lactic acid was found sourer than acetic.

In 10 observations lactic acid was found sourer than propionic.

In no observation was lactic acid found sourer than glycolic.

In 2 observations propionic acid was found sourer than glycolic.

In no observation was propionic acid found sourer than lactic.

Here the relation glycolic > lactic > acetic > propionic is not borne out by the relative differences in taste quite so decidedly as in the other series of acids already discussed. The difference between lactic acid and propionic is clearly shown by the taste, and so possibly also is the difference between glycolic and lactic. The difference in taste between glycolic and acetic, however, is not by any means so marked; in fact there was a good deal of confusion upon this point. According to one observer, however, who was exceedingly careful in arriving at conclusions respecting differences of taste, there was no doubt that glycolic was sourer than acetic, he having reached this conclusion after repeated trials on the taste of these two acids. So that taking all of these results into consideration, it is believed that judging entirely from differences in taste one would be justified in writing these acids in the following order of strength: glycolic > lactic > acetic > propionic.

In conclusion, it should be observed that the sour taste of acids is characteristic of a larger number of compounds than almost any other property that could be named as distinctive of any group of substances. Almost as many acids have a sour taste as redden litmus, or exhibit electrolytic dissociation in aqueous solution. As is well known, however, there are a few compounds which redden litmus, form salts, are more or less dissociated in aqueous solution, and which are ordinarily classed among the acids, that have not a sour taste. Such compounds are, for example, picric acid and benzoic sulphinide, the former of which is intensely bitter; the latter intensely sweet. Such instances, however, are exceedingly rare and do not seriously affect the general conditions of the problem. It would seem probable that the characteristic taste of such compounds as picric acid and benzoic sulphinide is due to the negative ion, the taste of which, in these compounds is so pronounced as to overcome that of the hydrogen ion altogether. This view derives support from the fact that the salts of such acids have the same taste as the acids themselves. The salts of benzoic sulphinide, for example, are sweet, those of picric acid are intensely bitter. In his study of the halogen substitution-products of benzoic sulphinide R. de Roode[1] observed that the calcium salts of *p*-fluor-, *p*-chlor-, *p*-brom-, and *p*-iodosulphinides have the same taste as the sulphinides themselves. On the other hand, it has been shown by Richards[2] that the *sour taste* of acids disappears completely on neutralization. The fact then that so very many acids are sour to the taste would of itself seem to indicate a close and intimate dependence of taste on the composition of this class of compounds, and if the sour taste is dependent on composition at all, then differences in composition ought at least to give rise to differences in the degree of sourness. The introduction of a strongly acidifying element or group into a weak acid, for example, ought to intensify the sour taste of the acid, in the same way, if not to the same extent, that it increases its electrical conductivity and its chemical affinity.

That such is indeed the case is shown especially in the comparisons made on the taste of monochloracetic and acetic acids, which are given in the above; and that the order of affinity of several acids can be approximately determined at least, by the sense of taste, seems scarcely to admit of doubt.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Feb., 1898.

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[1] This JOURNAL, **13**, 227.

[2] *Ibid*, **20**, 22.

THE ACTION OF NITRIC ACID ON TRIBROMACETANILIDE.

BY WILLIAM B. BENTLEY.

Introduction.

The attention of the writer was directed to this subject by the conflict between the accounts of tribromnitraniline (bromine atoms symmetrically placed) published by Körner[1] and confirmed by Nölting and Collin[2] and that given by Remmers[3]. The substance was made by Körner by brominating metanitraniline, and the constitution was confirmed by elimination of the amido group whereby he obtained the nitrotribrombenzol described by Jackson[4], thus proving the symmetrical position of the bromine atoms, and establishing the constitution of his compound. The product described by Remmers melted at 214°–215° instead of 102°.5, as given by the other investigators, and showed in other respects very different properties from those described by Körner. According to his description of his work, he converted ordinary tribromaniline into tribromacetanilide by the action of acetyl chloride. This tribromacetanilide was then converted into tribromnitracetanilide by action of nitric acid, and this was in turn saponified by heating with aqueous or alcoholic ammonia in a sealed tube to 180°–200°. This method of preparation left no doubt that, if a tribromnitraniline had been prepared as Remmers affirmed, it must be the same as that made by Körner, inasmuch as the bromine is symmetrically placed in tribromaniline, and could hardly have been transferred by any reaction which he described. Of course, it is obvious that two tribromnitranilines cannot be derived from symmetrical tribrombenzol. One point at which error seemed most likely was the saponification of nitrotribromacetanilide with ammonia. It appeared by no means improbable that a substitution-product had been formed in this way instead of the tribromnitraniline.

In view of these facts it seemed of sufficient importance to repeat the work of Remmers in order that the error might be detected and the facts correctly stated. In the work described below the author has found himself able to confirm less of Remmers' work than was at first expected. The tribromacetanilide was readily prepared but, though numerous methods were resorted to, a nitro derivative of this could in no way be obtained. Fuming nitric acid either had no action or produced an oily mass from which nothing crystalline was obtainable. With ordinary concentrated nitric acid (sp. gr. 1.38) several products were formed—tetrabrombenzol, a volatile oil of irritating odor (probably dibromdinitromethane), bromanil, oxalic acid and probably picric acid. If the nitric acid was dilute or was used in glacial acetic acid solution the products were the same as with concentrated nitric acid though they were apparently formed in different proportions. The only compound therefore described by Remmers which was capable of verification was tribromacetanilide.

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[1] Jsb. d. Chem., 1875, 347.

[2] Ber. d. chem. Ges., **17**, 266.

[3] *Ibid*, **7**, 351.

[4] *Ibid*, **8**, 1172.

In attempting to establish the identity of the bromanil formed by the reaction as above stated, the action of sodic phenylate was tried with the expectation of forming the dibromdiphenoxyquinone described by Jackson and Grindley[1]. The product of the reaction proved, however, to be quite different from Jackson and Grindley's compound. To make sure that this difference did not indicate that the substance used was other than bromanil this latter compound was prepared by the method of Stenhouse[2] but it gave the same compound that had been obtained before. This proves that with suitable modifications of the conditions of the reaction described by Jackson and Grindley bromanil yields a compound different from that obtained by these chemists. This compound was proved to be dibromdiethoxyquinone, a compound which is formed whenever bromanil is treated in absolute alcohol with sodic ethylate, sodic carbonate (anhydrous), potassic acetate, or oxide of silver. The difference between the conditions of the reaction described herein and the conditions of the reaction of Jackson and Grindley was found in the amount of water present, their reaction requiring the presence of water.

[1] Proc. Am. Acad., 30, 451.

[2] Ann. Chem. (Liebig) Suppl., 8, 13.

Experimental Part.

Tribromacetanilide was prepared in essentially the same way as was described by Remmers. Tribromaniline was dissolved in glacial acetic acid and acetyl chloride was added in excess. The mixture was boiled under a return-condenser until there was no further evolution of hydrochloric acid. On cooling, the tribromacetanilide crystallized out very nearly pure. The yield thus obtained was about 60 per cent. of the tribromaniline taken.

Action of Fuming Nitric Acid upon Tribromacetanilide.

Tribromacetanilide was covered with fuming nitric acid and left for six weeks standing in the laboratory at ordinary temperature. At first a slight evolution of red fumes was observed and the slightly gray color of the tribromacetanilide disappeared leaving the substance colorless. No further action was evident and, at the end of the time, the undissolved matter was separated and recrystallized, when it showed the melting-point 232° and was therefore unaltered tribromacetanilide. Two portions were next taken, covered with fuming nitric acid and heated, the one for a few minutes and the other for one-half hour, when they were cooled and diluted. The one which had been heated longer yielded a yellow solution containing a small quantity of oily matter, from which no crystalline product was obtainable. The other contained a small quantity of crystalline matter in addition to the oil and yellow solution. This was separated and recrystallized, when it melted at 227°, thus proving by the melting-point as well as by the crystalline form that it was unaltered tribromacetanilide. The experiments were varied by dissolving in glacial acetic acid and treating with fuming nitric acid, but the results were precisely similar to those described above. If the action was prolonged, a red, oily, unworkable mass was obtained while, if the reaction was interrupted sooner, there was found, in addition to the other products, a small quantity of unaltered tribromacetanilide. From these experiments it was decided that fuming nitric acid gave a nitro derivative such as was described by Remmers under no conditions that could be found. It is interesting in this connection to note the results obtained by Losanitsch[1] from the action of nitric acid on tribromaniline. They may be summarized as follows: When tribromaniline is boiled with concentrated nitric acid, dibromdinitromethane distils over and tetrabrombenzol remains in the flask together with bromanil, oxalic acid, and picric acid. When nitric acid acts upon tribromaniline in glacial acetic acid solution the same products are formed; if, however, the heating of the mixture is stopped when red fumes begin to come off, dibromnitraniline is formed. The author has repeated the experiments of Losanitsch, and finds that dibromnitraniline is formed without great difficulty by heating a glacial acetic acid solution of tribromaniline with either concentrated or fuming nitric acid until the solution becomes yellow. The difference between the behavior of tribromaniline and the acetyl derivative when treated in glacial acetic acid solution with nitric acid is noteworthy, in view of the similarity of their behavior when treated with concentrated nitric acid alone.

Action of Concentrated Nitric Acid on Tribromacetanilide.

Having failed to reproduce Remmers' work with fuming nitric acid, ordinary concentrated nitric acid was next tried. The mixture was boiled, causing the evolution of dense red fumes and giving another substance of most irritating odor which, it should be observed, was also formed in smaller quantity in the experiments with fuming nitric acid above described. Small needle-shaped crystals were noticed in the neck of the flask, and the liquid was yellow and contained a yellow crystalline substance, as well as some gummy matter. A retort was then substituted for the flask, and the acid, carrying with it the volatile products of the reaction, was continuously distilled off, being renewed from time to time by the addition of fresh acid. The distilled acid contained a considerable volume of white, silky-looking crystals, and a yellow oil. This white compound, although it appeared considerable, was really but very little, and a great deal of material was used in getting sufficient for purification and analysis. Although Losanitsch obtained this compound (tetrabrombenzol) from the undistilled portion, in this case such a method of procedure was not successful. After distilling for a short time, there was a gummy mass, from which tetrabrombenzol was not obtained by crystallization, but it did yield this compound by further distillation as has been said. It seemed probable that this gummy mass was chiefly undecomposed tribromacetanilide mixed with some oily decomposition-product (derived possibly from the acetyl group), which was by further treatment entirely destroyed. The distilled crystalline matter was repeatedly recrystallized from alcohol, and had the melting-point 92°. Recrystallization did not raise this melting-point. It was dried in the desiccator and analyzed with the following results:

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[1] Ber. d. Chem. Ges., **15**, 471.

I. 0.2321 gram of the substance gave on combustion 0.1542 gram of carbonic dioxide and 0.0141 gram of water.[1]

II. 0.1855 gram of the substance gave by the method of Carius 0.3341 gram of argentic bromide.

	Calculated for $C_6H_2Br_4$.	Found.	
		I.	II.
C	18.27	18.12	....
H	0.51	0.67	....
Br	81.21	....	81.23

These analyses leave no doubt that the substance was tetrabrombenzol in a fair state of purity in spite of the fact that Körner[2] gives the melting-point of this substance as 98.5°. This discrepancy in the melting-point of tetrabrombenzol recalls a similar discrepancy in the melting-point of tetrabromdinitrobenzol. This substance was made by Richter[3] by action of nitric acid on tetrabrombenzol, and he gives the melting-point 227°–228° The same compound was made by Jackson and Wing[4] by action of a mixture of fuming nitric and sulphuric acids on tribromdinitrobenzol but the melting-point could not be raised above 224°. This low melting-point was attributed to the presence of a small amount of tribromtri (or di)nitrobenzol and it is possible that the low melting-point of the tetrabrombenzol is due to the same cause.

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[1] I wish here to acknowledge my obligations to Professor W. S. Hendrixson, of Iowa College, and his assistant, who made the analyses in this paper for me, since, at the time this work was done, the limited facilities for organic analysis in this laboratory prevented me from making them myself.

[2] Jsb. d. chem., 1875, 343.

[3] Ber. d. chem. Ges., 8, 1427.

[4] This JOURNAL, 10, 291.

It is worth noting that these low-melting compounds were formed by similar methods, acting upon a tribrombenzol with an acid which causes decomposition.

As has been mentioned, there was also formed in the reaction just described, a yellow crystalline substance which remained after the acid had been distilled off. This compound was, however, formed only in very minute quantities and as it was found possible to modify the conditions so as to secure a fair quantity of this compound, no attempt was made to get from this reaction anything but the tetrabrombenzol already described.

Action of Dilute Nitric Acid on Tribromacetanilide.

It was found that if dilute nitric acid was used and the mixture boiled for a longer time the liquid became yellow and the same irritating odor was perceptible. Tetrabrombenzol also distilled off, but owing to its being less volatile with steam than with nitric acid or to a smaller yield of this compound in this reaction, much less of the tetrabrombenzol was obtained here. The yellow crystalline product was, however, in much larger quantity than before. Numerous experiments were made to find the conditions most favorable for the production of this yellow compound, and the following method gave the most satisfactory results: 15 grams of tribromacetanilide was heated with 150 cc. of 80 per cent. acetic acid and 150 cc. of concentrated nitric acid (sp. gr. 1.4) was gradually added. Complete solution did not take place, but the tribromacetanilide was gradually replaced by the yellow compound in a crystalline and fairly pure condition. The yield was about 35 per cent. of the tribromacetanilide taken The compound was found to be very sparingly soluble in hot alcohol, from which it crystallizes in yellow scales which did not melt at 300°, though it sublimed as low as 260°. Bearing in mind the results obtained by Losanitsch it seemed probable that this compound was bromanil, a conclusion which was supported by the agreement between its properties and those of bromanil. In order further to test the similarity of this reaction to that of Losanitsch, some of the yellow acid liquid, from which bromanil had been precipitated, was neutralized with calcic carbonate, when a yellow precipitate was formed. This precipitate dissolved in hydrochloric, and from this solution a white precipitate was thrown down upon addition of ammonic hydrate, the coloring-matter having been left in solution. The precipitate was insoluble in acetic acid and gave carbonic dioxide when treated with manganese dioxide and sulphuric acid. This was, therefore, calcic oxalate, and oxalic acid was a product of this reaction, as it was of the reaction of Losanitsch. The main product of Losanitsch's reaction was dibromdinitromethane, and the properties of this compound were identical with those of the yellow oil obtained in all these experiments so far as the latter were observed. No particular study was given to this compound, because of the unpleasant properties of the substance and because it had been very thoroughly studied by Losanitsch. The remaining compound obtained by Losanitsch was picric acid. At no time was any considerable quantity of picric acid obtained in these experiments, though the yellow color of all of the solutions may have been due to very small quantities of this compound. No definite proof of its formation was obtained as the yellow matter which colored the solutions was in too small quantity to yield anything definite.

Dibromdiethoxyquinone.

In order to prove that the yellow compound was bromanil, it was treated with sodic phenylate according to the directions of Jackson and Grindley. Two grams of the substance were treated with an absolute alcoholic solution of sodic phenylate prepared by acting upon absolute alcohol with 0.3 gram sodium and adding 3 grams phenol. The reaction began immediately after the phenylate came in contact with the bromanil, and the solution became deep red. To insure the completion of the reaction, the mixture was gently warmed, when the bromanil gradually disappeared and was replaced by a white precipitate. The solution was filtered, but no solid matter was obtained except the white substance which was shown to be sodic bromide. It is at this point that the first difference between this reaction and that of Jackson and Grindley was noticed, as their organic product was not dissolved by the alcohol in which the reaction was carried on. The red alcoholic solution was diluted with water, when a red crystalline precipitate separated. This compound was made, it should be said, by using bromanil, made by the method of Stenhouse, as well as from the bromanil prepared in the reaction described above, and these observations were taken as proof that the compound assumed to be bromanil was in fact nothing else. The compound which had been precipitated with water was recrystallized from alcohol and analyzed with the following result:

0.2242 gram of the substance gave by the method of Carius 0.2363 gram of argentic bromide.

	Calculated for $C_6O_2Br_2(OC_2H_5)_2$	Found.
Br	45.19	44.86

This compound was also prepared by acting on bromanil with absolute alcohol and potassic acetate (anhydrous). This reaction yielded about 50 per cent. of the theoretical amount. The compound was also made when bromanil was boiled with sodic carbonate and absolute alcohol. This method of preparation was the most suitable for the preparation of the compound, as the yield was better than that of any other method, and the compound was essentially pure. It was also possible to prepare this substance by treating bromanil with sodic ethylate, but there was much oily matter produced, no doubt by a subsequent action of the excess of reagent on the main product in a manner similar to that observed by Jackson and Grindley in the case of dibromdiphenoxyquinone and sodic methylate. Bromanil was boiled with argentic oxide and absolute alcohol and the same compound was found as in the reactions described above, but in this case prolonged boiling was required and the yield was very small. These numerous methods of preparation as well as the analysis recorded above, show conclusively that the compound is dibromdiethoxyquinone. In this connection it is perhaps of some importance to record two negative results. Bromanil was boiled with absolute alcohol and calcic hydrate, also with absolute alcohol and baric hydrate, but in neither case did any reaction take place.

Properties of Dibromdiethoxyquinone.—It crystallizes from alcohol in orange-red prisms with square ends. These prisms appear to be square and to belong to the trimetric system. The melting-point is 139°. It is freely soluble in ethyl or methyl alcohol when hot but much less soluble in cold alcohol. It is soluble in ether, glacial acetic acid, and carbonic disulphide, and very freely soluble in cold benzol, chloroform, and acetone. In water it is insoluble either cold or hot. It dissolves in concentrated nitric or sulphuric acid, but does not appear to undergo any reaction. From the hot nitric acid solution, it crystallizes on cooling. Concentrated hydrochloric acid has no action on it, but it reacts with potassic hydrate or aniline, and is by glacial acetic acid and zinc dust reduced to a colorless compound presumably the corresponding hydroquinone. None of these reactions have however been studied.

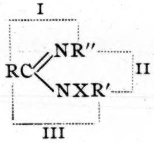
Experiments were next made to determine the modification of conditions necessary in order to produce the dibromdiphenoxyquinone instead of the diethoxy compound, and it was found that if ordinary 95 per cent. alcohol was used instead of absolute alcohol, the product did not dissolve in the alcohol used in the experiment, and when it was filtered out showed by the melting-point and other properties that it was the compound described by Jackson and Grindley, dibromdiphenoxyquinone. It should be remarked that the analysis quoted above shows by the low percentage that the analyzed sample contained a small quantity of dibromdiphenoxyquinone that could not be removed by recrystallization. The melting-point did not differ perceptibly from that of the compound prepared by different reactions where it could not contain any of the diphenoxy compound. These results make it possible to extend and slightly modify the observations of Jackson and Grindley regarding the difference of behavior of sodic phenylate towards chloranil and bromanil. They find that chloranil when treated with aqueous sodic phenylate substitutes two phenoxy groups for two chlorine atoms ; with alcoholic sodic phenylate all four chlorine atoms are replaced, two with phenoxy groups and two with ethoxy groups. Bromanil on the other hand gives with an alcoholic solution of sodic phenylate, if a small percentage of water is present, diphenoxy derivative, while, if the sodic phenylate is dissolved in absolute alcohol instead, a diethoxy derivative results.

Contributions from the Sheffield Laboratory of Yale University.

LX.—RESEARCHES ON THE CYCLOAMIDINES: PYRIMIDINE DERIVATIVES.

By H. L. Wheeler.

For convenience of reference, in this work, those compounds which have the amidine formation



in which two of the radicals R, R′, and R″ are replaced by a ring structure or a bivalent grouping, are referred to as cycloamidines. The dotted lines in the above formula show the three possible ways of replacing the radicals, and they indicate three forms of cycloamidines. It will be noticed, however, that III is the tautomeric form of I. The tautomeric form of II being obtained when the position of the hydrogen X is changed to the opposite nitrogen atom. There are therefore only two types of cycloamidines, each type having a pseudomeric or tautomeric form as in the case of the simple amidines.

The *first type*, which contains only one of the nitrogen atoms in the ring is represented by such compounds as α-aminoquinoline, the α-aminobenzoxazines, etc.

The *second type*, with both nitrogen atoms in the ring structure, is found in the anhydro bases, glyoxalines, lophin, etc.

Then, further, combinations of these types and their tautomeric forms occur: The cyanalkines, α-amino- and anilidopyrimidines, aminoquinoxalines, cyanuramide, dicyanorthophenylenediamines, and the like, are examples of the combination types.

The object of the work, of which this paper gives a preliminary account, is primarily to investigate the action of alkyl halides on some of these cycloamidines which have not yet been examined in this respect, and also to compare this action in general with that of the simple amidines.

Pechmann[1] assumes that when a simple amidine, represented by the general formula above, is acted on with alkyl iodides, the hydrogen X is directly replaced, and hence this reaction serves to determine structure.

It seems to the writer that alkyl iodides may be added either to the amido group or to the imido group or, when the substituents are similar,[2] to both and perhaps to the atoms joined by double union. In two of the latter cases an amidine would result of a different structure from that obtained by direct substitution, so that this method of determining structure seems to be not without objection.

The cycloamidines, in general, unite with alkyl iodides and a number of cases have been described among those of the first type, where no direct substitution or replacement of hydrogen in the amino group takes place, at least not as the first step of the reaction. To illustrate this the following may be cited: Thiele and Ingle[3] obtained dialkylaminotetrazols by the action of alkyl iodides on aminotetrazol. They believe that in these only one of the alkyl groups replaces hydrogen of the amino group. Claus[4] shows that α-aminoquinoline takes up alkyl iodides in the same manner as the quinoline and pyridine bases in general, and that the amino-hydrogen is not substituted. Again, E. v. Meyer[5] has shown in several cases that the cyanalkines form similar addition-products, the amino group not being substituted.

Even acyl chlorides add to the cyanalkines without substituting the amino group. Herfeldt[6] found that cyanbenzylin or aminophenyldibenzylmiazin unites with acetyl and benzoyl chlorides to form well crystallized addition-products, and that an acetyl or benzoylcyanbenzylin was not obtained. In these cases it is a tertiary nitrogen which is the point of attack or addition.

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[1] Ber. d. chem. Ges., **28**, 2362 and 869.

[2] Pechmann (*loc. cit.*) found that when the substituents are similar radicals, the amidine gave two isomeric alkylated products. This is precisely what would be expected if the action is one of addition. There being in that case no decided tendency to addition entirely to either one of the nitrogen atoms.

[3] Ann. Chem. (Liebig), **287**, 249.

[4] J. prakt. Chem., **17**, 209.

[5] *Ibid.* **22**, 266, and **39**, 265.

[6] *Ibid.* [2], **53**, 249.

The action of alkyl iodides on the cycloamides of the second type is that of addition also, and, as in the case of the simple amidines, this action has generally been considered to be a direct replacement of hydrogen, since by treating the addition-product with alkali alkyl compounds result. The same question arises here as in the case of the simple amidines. That the alkyl group invariably replaces the hydrogen, however, has not been proved. It is not improbable that, like the cycloamidines of the first class, it is the tertiary nitrogen that unites with the alkyl halide.

The writer has found that phenylmethylanilidopyrimidine acts with methyl and ethyl iodides forming stable addition-products, and that no substitution takes place, that the alkyl iodide unites with one of the tertiary nitrogen atoms of the ring and not with the anilido group follows in all probability from the behavior of these products with alkali :

$$C_{17}H_{15}N_3.CH_3I + NaOH = C_{17}H_{15}N_3 + CH_3OH + NaI.$$

That is, methyl alcohol and sodium iodide are quantitatively formed, and unaltered anilidopyrimidine is regenerated. The formula that appears most probable for these addition-products is therefore either I or II, and from analogy a similar structure might be expected in the case of the alkyl halogen addition-products of the simple amidines.[1]

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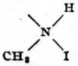
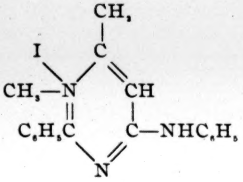
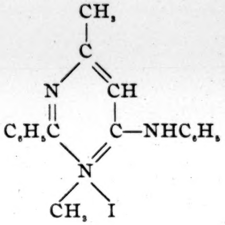
[1] The fact that the alkyl iodide addition-products of the simple amidines give up hydrogen iodide and not the alkyl group as above cannot be considered as showing that the addition takes place to the —NH— group of the amidine. To be sure, the grouping 

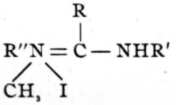
would be expected to give up hydrogen iodide, and those alkyl iodide addition-products of the cyloamidines which do not separate hydrogen iodide most probably do not have this grouping. But it cannot be maintained that because an addition-product gives up hydrogen iodide, it has this grouping.



I



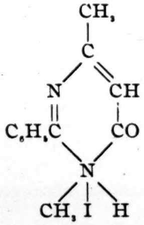
II



III

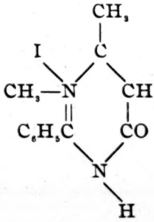
This being the case, the structure of the simple amidines must be completely revised, and the opposite or so-called tautomeric structure must be assigned to them. At any rate, no method has yet been devised for determining the structure of the amidines in question that is without objection.

It will be shown below that phenylmethylpyrimidon, a cycloamidine of the second type, unites with one molecule of methyl iodide to form a beautiful crystalline addition-product of formula IV or V.



IV

or



V

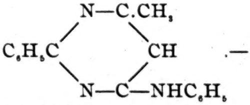
This compound, on treatment with alkali, gives up hydrogen iodide and not the alkyl group, and an alkylated pyrimidon results. This alkyl derivative differs decidedly from the product obtained by heating phenylmethylchlorpyrimidine with sodium methylate. The alkyl iodide therefore is added to one of the nitrogen atoms of the pyrimidon ring, while Pinner[1] found that, if the oxypyrimidine is heated with ethyl iodide in the presence of alkali, the ethyl group attaches itself to oxygen.

In order to determine to which nitrogen the alkyl halide is added, a synthesis of the methylpyrimidon was attempted as follows: Methylbenzamidine hydrochloride was prepared. This, with acetoacetic ester, according to Pinner's explanation of the formation of the pyrimidines, might be expected to give the base corresponding to formula IV. It was found, however, that methylbenzamidine does not give a pyrimidine derivative with acetoacetic ester, at least not under the same conditions that benzamidine does, so that for the present the question of the position of the alkyl group must be left undecided.

Nef[2] has shown that carbostyril is not acted on by ethyl iodide. The above pyrimidon differs from carbostyril, in its ring structure, in having a tertiary nitrogen. It would seem most probable therefore that it is due to this that the substance takes up methyl iodide and that the addition-product is perhaps best represented by formula V.

Experimental Part.

Phenylmethylanilidopyrimidine,



.—This was prepared according to Pinner's[3] directions by warming phenylmethylchlorpyrimidine with aniline. Instead of purifying the material by dissolving the reaction-product in alcohol and precipitating it with ether, it was found best to crystallize it directly from water, precipitate the base from the hot aqueous solution and then crystallize this from benzene and alcohol. The material thus obtained crystallizes in clusters of small prisms and melts at 160°–161°. Pinner gives its melting-point as 150°–153°.

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[1] Die Imidoäther und ihre Derivate, p. 343.

[2] Ann. Chem. (Liebig), **276**, 242.

[3] Die Imidoäther und ihre Derivate, p. 248.

The *hydrochloride* was obtained in colorless needles melting at 240° as described by Pinner.

The *hydrobromide* was obtained by precipitating the base from a benzene solution with hydrobromic acid gas. It forms minute needles when crystallized from alcohol and it melts at 250°.

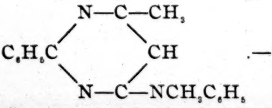
The *hydroiodide* forms colorless needles melting at 231°.

Phenylmethylanilidopyrimidine methyl iodide.—Six grams of the above cycloamidine were heated with an excess of methyl iodide in methyl alcohol solution for seven hours from 100°–105°. The material was then washed with alcohol and crystallized from water and alcohol. Thus obtained, the substance melts at about 210°–213° with strong effervescence. If suddenly heated it melts much lower. The material dried in the air contains 2 molecules of water of crystallization. [Analysis I. and II.] When dried at a temperature of 130° it was obtained anhydrous [Analysis III.]. Determinations I. and III. were made by dissolving the substance in water and precipitating with silver nitrate. Determination II. was made by the method of Carius.

	Calculated for		Found.		
	$C_{18}H_{18}N_3I.2H_2O$.	$C_{18}H_{18}N_3I$.	I.	II.	III.
I	28.9	31.5	28.8	28.7	31.5

This addition-product is readily soluble in warm water and in alcohol, from which it crystallizes in fine, colorless needles. Ammonia or alkali immediately precipitates a substance melting at 160°–161°, which has all the properties of phenylmethylanilidopyrimidine.

Phenylmethylmethylanilidopyrimidine,



.—This was prepared by warming phenylmethylchlorpyrimidine with methyl aniline. It is the compound that should result by treating the above addition-product with alkali, if the action of methyl iodide on the cycloamidine takes place by substitution. A comparison of the above with the following properties show that these compounds are different. This compound crystallizes from alcohol in colorless prisms which melt at 113°. It dissolves readily in ether, alcohol, and benzene, but is insoluble in water. A nitrogen determination gave:

	Calculated for $C_{18}H_{17}N_3$.	Found.
N	15.2	15.0

This compound dissolves readily in dilute hydrochloric acid, and platinum chloride gives a bright yellow, granular precipitate, which melts at about 228°, with effervescence.

The *hydroiodide* is readily soluble in warm alcohol, less readily in water. It melts when slowly heated at about 198°. An iodine determination gave:

	Calculated for $C_{18}H_{18}N_3I.2H_2O$.	Found.
I	28.9	28.9

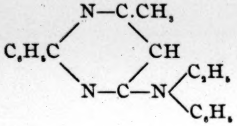
The *nitrate* separates from dilute nitric acid in long, colorless needles or prisms, which melt with violent effervescence at about 170°.

Phenylmethylanilidopyrimidine ethyl iodide.—This was obtained when 5 grams of phenylmethylanilidopyrimidine were heated with 10 grams of ethyl iodide for twelve hours at 120°–130°. The reaction-product was extracted with hot water and then crystallized from alcohol, when it separated in colorless needles melting at about 215°. When crystallized from water the material shrivels at about 115°, then melts with effervescence at or near 215°. An iodine determination of air-dried material indicates that the substance separates with 1 molecule of water of crystallization. [Analysis I.] The material dried at 120°–130° becomes anhydrous. [Analysis II.]

	Calculated for		Found.	
	$C_{19}H_{20}N_3I.H_2O$.	$C_{19}H_{20}N_3I$.	I.	II.
I	29.19	30.4	29.24	30.3

This addition-product and the analogous methyl compound give off the methyl iodides when heated to their melting-points. Ammonia or alkali precipitate phenylmethylanilidopyrimidine from aqueous or alcoholic solutions.

Phenylmethylethylanilidopyrimidine,



.—This was prepared like the corresponding methylanilidopyrimidine for the sake of comparison with the base obtained from the above addition-product. It is an entirely different base. This melts at 87° when crystallized from alcohol. It is readily soluble in hot alcohol, difficultly in cold, and insoluble in water. It separates in beautiful, long, colorless prisms. A nitrogen determination gave :

	Calculated for $C_{19}H_{19}N_3$.	Found.
N	14.53	14.56

The *hydrochloride* is difficultly soluble in cold water, readily in hot, and crystallizes in colorless needles which appear to be hydrous. On heating the material shrivels at about 100°, then melts at about 210°.

The *platinum chloride salt* separates as a bulky, light-yellow precipitate. It is insoluble in hot water, and melts at about 218°.

The *hydroiodide* crystallizes in prisms.

An attempt to prepare an ethyl bromide addition-product of phenylmethylanilidopyrimidine was unsuccessful. 3.8 grams of anilidopyrimidine were heated with an excess of ethyl bromide from 102°–104° for five hours, when the material was found to be unaltered. It was heated again, this time with the addition of some alcohol, the temperature being kept between 120°–130° for seventeen hours. On opening the tube then, the products were found to be the hydrobromide of phenylmethylanilidopyrimidine described above, and ether. Ethyl bromide, therefore, neither effects substitution nor addition.

Phenylmethylpyrimidon methyl iodide.—Phenylmethyloxypyrimidine and methyl iodide, 4 grams of the former and 10 of the latter, were heated for six hours at 100°. No reaction was evident. The material was then heated for nine hours at

170°, when addition took place. The material dissolved almost entirely in water and, on concentrating the aqueous solution to a syrup, a mass of needles was obtained. This was crystallized from alcohol when beautiful, large, colorless prisms separated. These did not melt sharply, but decomposed with effervescence at 230°. An iodine determination gave:

	Calculated for $C_{11}H_{10}N_2O.CH_3I$.	Found.
I	38.7	38.6

n-Methylphenylmethylpyrimidon.—When the above compound with methyl iodide was dissolved in a little water and dilute alkali was added, this compound separated as a mass of colorless needles. It was purified by crystallizing from water, when it separated in the form of beautiful, large prisms, which melt at about 91°–92°. A nitrogen determination gave:

	Calculated for $C_{12}H_{12}N_2O$.	Found.
N	14.0	13.6

This compound has basic properties; it dissolves readily in dilute acids, the ordinary salts being all quite soluble. It is readily soluble in alcohol and ether, less readily in water, and is not dissolved by a small amount of alkali. The nitrate and platinum chloride double salt are the least soluble of the ordinary salts. These were obtained by spontaneous evaporation of the solutions.

The *nitrate* crystallizes in colorless, flattened prisms which melt with effervescence at about 195°.

The *platinum chloride* double salt separates in form of very large prisms with the color of azobenzene. It gave no definite melting-point below 275°, but turned dark at about 235°.

Methylbenzamidine hydrochloride, $C_6H_5C(NH)NHCH_3.HCl$.—This was prepared by dissolving benzimidoethylester hydrochloride in a 33 per cent. solution of methylamine. On adding the hydrochloride to the solution of the amine the free ester separates; on shaking this dissolves, and in a short time a mass of colorless needles separates. This material was crystallized from water in which it is not extremely soluble. A chlorine determination gave:

	Calculated for $C_8H_{10}N_2.HCl$.	Found.
Cl	20.82	20.75

The properties of this amidine hydrochloride apparently differ decidedly from those of the corresponding ethylamidine. Lossen[1] prepared ethylamidine hydrochloride in a state of purity only with some difficulty, while Pinner[2] obtained the hydroiodide as an oil which would not crystallize.

NEW HAVEN, March, 1898.

SOME DOUBLE SALTS CONTAINING SELENIUM.

BY JAMES F. NORRIS.[3]

INTRODUCTION.

A large number of double halides containing the aliphatic amines has been prepared. These show greater complexity than the double salts of ammonium or the alkali metals. Where all the possible combinations have been determined, the series of salts found are more complete, and a greater variety in composition is exhibited. For example, bismuth forms the following iodides[4] with dimethylamine:

$$2BiI_3.3(CH_3)_2NH.HI,$$
$$3BiI_3.4(CH_3)_2NH.HI,$$
$$3BiI_3.5(CH_3)_2NH.HI.$$

Copper has the complete series:[5]

$$CuCl_2.(CH_3)_2NH.HCl,$$
$$CuCl_2.2(CH_3)_2NH.HCl,$$
$$CuCl_2.3(CH_3)_2NH.HCl.$$

And, finally, the following double chlorides of mercury[6] have been described:

$$5HgCl_2.(CH_3)_3N.HCl,$$
$$2HgCl_2.(CH_3)_3N.HCl,$$
$$HgCl_2.(CH_3)_3N.HCl,$$
$$HgCl_2.2(CH_3)_3N.HCl.$$

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[1] Ann. Chem. (Liebig) **265**, 159.

[2] Ber. d. chem. Ges., **11**, 7.

[3] From the Author's Dissertation submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

[4] Ann. Chem. (Liebig), **210**, 310.

[5] Jsb. d. Chem., 1883, 618.

[6] *Ibid.*, 1883, 618.

The general conclusion that the double halides containing the substituted ammonias are more complex than those containing ammonia and the alkali metals is strengthened by the results of the investigation of the selenium compounds. The influence of the introduction of alkyl groups on the stability of the halides of selenium is noticeable. Selenium tetrachloride is decomposed by water, and, even in the presence of strong hydrochloric acid, is not capable of entering into a double salt with ammonium chloride. Muthmann and Schäfer,[1] in their study of the double halides of selenium and ammonium, found that the only chloride possible was one of the composition $2SeO_2.NH_4Cl.2H_2O$, in which there is a complete breaking down of the selenium tetrachloride.

The work on the compounds containing dimethyl- and trimethylamine brings out the fact that owing to the presence of these bases, selenium can enter into combination as the oxychloride, $SeOCl_2$, where the molecule of the tetrachloride has undergone only half decomposition. The salts $SeOCl_2.(CH_3)_3N.HCl$ and $2SeOCl_2.3(CH_3)_2NH.HCl$ were obtained, when concentrated hydrochloric acid was the solvent. If the trimethylamine salt is recrystallized from dilute acid, one-half of the selenium oxychloride is changed into the oxide, and the salt $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$ is obtained.

Double salts containing selenium oxychloride are not unknown. Weber[2] prepared the following salts by mixing the oxychloride with the chlorides of the respective metals: $2SeOCl_2.SnCl_4$, $2SeOCl_2.TiCl_4$, $2SeOCl_2.SbCl_5$.

The bromides about to be described also show greater complexity than those containing ammonium. With ammonium bromide Muthmann and Schäfer succeeded in making the compound $SeBr_4.2NH_4Br$, while with both dimethyl- and trimethylamine four double bromides have been obtained.

The study of a salt containing selenium oxybromide, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, led to an interesting class of double salts containing selenium and perbromides of dimethyl- and trimethylamine. An attempt was made to replace the oxygen in the above compound by crystallizing it from a solution containing a large quantity of free bromine. The salt $SeBr_4$.-

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[1] Ber. d. chem. Ges., **26**, 1008.

[2] Pogg. Ann., **125**, 325.

$(CH_3)_3N.HBr$ would thus result. This was not obtained, but a well-characterized compound, which dissolved in water with evolution of bromine. Two explanations of the action of the bromine were possible: either the selenium, in the presence of such a strong oxidizing agent, entered into combination in the hexavalent state with the formation of the salt $SeBr_6.2(CH_3)_3N.HBr$, or the bromine attacked the trimethylamine hydrobromide part of the compound. If the first view were the correct one, such a salt should be possible with ammonium bromide. Accordingly, the ammonium salt was made and crystallized from a solution containing bromine. The original compound, $SeBr_4.2NH_4Br$, resulted. Trimethylamine hydrobromide was next crystallized from a solution containing free bromine. A new compound, having the formula $(CH_3)_3N.HBr.Br$, was obtained, which dissolved in water with the liberation of the halogen. Analogous perhalides of other aliphatic amines have recently been described.[1]

It was the intention to study the series of salts formed by mono-, di-, and trimethylamine, and to observe in what way the increase in the number of methyl groups affected the compounds. The great wealth of material found and the difficulties encountered rendered the investigation of the di- and trimethylamine compounds alone possible. With these, interesting differences have been observed, but the series must be completed before any general conclusions can be drawn.

The double salts described in the following pages are tabulated below:

With Trimethylamine, $(CH_3)_3N$.

The Chlorides:

$SeOCl_2.(CH_3)_3N.HCl$.
$SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.

The Bromides:

$SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$.
$SeBr_4.2(CH_3)_3N.HBr$.
$SeBr_4.2[(CH_3)_3N.HBr_2]$.
$SeBr_4.1[(CH_3)_3N.HBr_2].(CH_3)_3N.HBr$.

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[1] This JOURNAL, 20, 51.

With Dimethylamine, $(CH_3)_2HN$.

The Chlorides:

$2SeOCl_2.3(CH_3)_2HN.HCl$.
$SeO_2.(CH_3)_2NH.HCl$.

The Bromides:

$2SeBr_4.SeBr.3(CH_3)_2HN.HBr$.
$SeBr_4.2(CH_3)_2HN.HBr$.
$SeBr_4.2[(CH_3)_2HN.HBr_2]$.
$SeBr_4.2[(CH_3)_2HN.HBr_2].(CH_3)_2HN.HBr$.

Methods of Analysis.

Selenium.—The double salts about to be described differed markedly in their action toward water. Some dissolved to a clear solution, others gave off free bromine, and still others went into solution with precipitation of selenium. The methods of analysis had to be varied, accordingly, to suit each particular case.

In the first part of the investigation, when the trimethylamine salts were studied, the selenium was determined gravimetrically. The salt was dissolved in water, sodium sulphite added, and then an excess of strong hydrochloric acid. It is necessary to have the solution acid, as an excess of sodium sulphite prevents the complete precipitation of the selenium. The solution was heated to incipient boiling until the selenium sank to the bottom of the vessel as a black powder. The precipitate was filtered into a weighed Gooch crucible and dried at 90° for two hours. This method yielded excellent results, although in most cases the amount of selenium weighed was small.

A more rapid method was desirable and, accordingly, that devised by Muthmann and Schäfer[1] was tried. As this did not give satisfactory results a new method was used, based on the reaction between sodium thiosulphate and selenium dioxide in acid solution. An account of the method has already been published.[2]

Selenium was precipitated when some of the compounds were dissolved in water. It was necessary to determine in these cases the selenium precipitated as well as the total amount. The total selenium was determined gravimetrically as described above. That which went into solution as selenium dioxide was next determined by the volumetric method in another portion, and the precipitated selenium found by difference. This method gave better results than weighing the precipitated selenium directly, as the amount set free was usually very small.

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[1] Ber. d. chem. Ges., **26**, 1008.

[2] Norris and Fay: This JOURNAL, **18**, 703.

The determination of the selenium in the compounds which gave off bromine was made gravimetrically. At first the bromine was removed by passing steam through the solution and titrating, but this method did not yield as accurate results as the gravimetric, which was accordingly used.

Halogens.—At first the gravimetric method was used for the determination of the halogens. The precipitation was made in the usual way and the precipitate filtered off while the solution was still hot, because, if allowed to cool, silver selenite crystallized out. The results came usually low when the precipitate was filtered off as soon as the solution had cleared up. It was found advisable to let the solution cool, and when the precipitate had become granular, to heat just to boiling before filtering.

The large number of analyses which had to be made rendered a quicker method desirable. The Volhard method was tested, therefore, to see if the selenium in the compounds would interfere with the accuracy of the results. When the ferric ammonium alum is added to the solution of the salt a precipitate is formed. If slightly more dilute nitric acid than is required to clear up the solution is added, the precipitation of the halogen takes place normally and the selenium compound remains dissolved. The method was tested. A weighed quantity of potassium chloride was dissolved in water containing selenium dioxide and the chlorine determined.

I. 0.1614 gram KCl gave 0.0766 gram Cl.

II. 0.2202 gram KCl gave 0.1044 gram Cl.

	Calculated for KCl.	Found.	
		I.	II.
Cl	47.54	47.46	47.42

As stated, some of the salts gave off free bromine when dissolved in water. It was necessary to determine both the bromine set free and the total halogens in the compounds. To find the latter, the salt was weighed into a dry beaker and a dilute solution of sulphur dioxide carefully added. As the bromine was liberated it was reduced. In this solution the hydrobromic acid was determined by titration with a solution of silver nitrate. To determine the free bromine the salt was weighed into a dry glass-stoppered bottle and potassium iodide and water added. The iodine set free was that equivalent to the bromine plus that liberated by the selenium dioxide. The latter was calculated from the percentage of selenium in the compound, and the amount equivalent to the bromine found by difference. It is necessary to add a small quantity of hydrochloric acid in order to liberate the hydriodic acid, which reacts with the selenium dioxide.

The halogen in the compounds which dissolved with precipitation of selenium was determined volumetrically in the filtered solution.

TRIMETHYLAMINE SALTS.

The Chlorides.

Salt of the Composition $SeOCl_2.(CH_3)_3N.HCl$.—Selenium tetrachloride and trimethylamine hydrochloride were brought together in strong hydrochloric acid in proportions varying from three to one of the former to one to three molecules of the latter and the solution left to crystallize in a desiccator. After standing about six weeks crystals appeared, quite pure in the solutions containing an excess of selenium, but in the other beakers mixed with trimethylamine hydrochloride. The double salt was separated mechanically and proved to be the same compound which was obtained in pure condition in the solution in which the constituents had been mixed in the proportion of 2 molecules of selenium tetrachloride to one of trimethylamine hydrochloride.

The salt is exceedingly soluble in water, hydrochloric acid, and alcohol. It must be obtained by slow evaporation, for if an attempt is made to concentrate the solution by heat, a thick sirup is formed. The salt is insoluble in ether, but dissolves in a mixture of alcohol and ether, the solubility increasing with the amount of the former. A mixture of equal parts of alcohol and ether containing concentrated hydrochloric acid is the best solvent from which to crystallize. Notwithstanding its great solubility, it can be obtained in well-defined crystals. These are colorless, monoclinic plates, elongated in the direction of the orthodiagonal axis. A careful examination was impossible, as the salt is very hygroscopic.

Two samples were analyzed with the following results :

I. 0.3154 gram salt gave 0.0946 gram Se.
II. 0.1874 gram salt gave 0.0565 gram Se.
III. 0.2263 gram salt gave 0.3693 gram AgCl.
IV. 0.1985 gram salt gave 0.3254 gram AgCl.

	Calculated for $SeOCl_2.(CH_3)_3N.HCl$.	Found.			
		I.	II.	III.	IV.
Se	30.23	30.00	30.15	....	....
Cl	40.64	....	....	40.36	40.55

Salt of the Composition $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.—Muthmann and Schäfer, working with the double salts containing selenium and ammonium, discovered that the only chloride possible was one of the composition $2SeO_2.NH_4Cl.2H_2O$. With trimethylamine hydrochloride in strong hydrochloric acid, the decomposition of the selenium tetrachloride did not go so far, for selenium oxychloride, $SeOCl_2$, entered into combination. An attempt was accordingly made to get a salt analogous to that made by Muthmann and Schäfer. Selenium tetrachloride and trimethylamine hydrochloride were crystallized from dilute hydrochloric acid. A mixture of two salts was obtained. In order to get the second chloride in pure condition, selenium tetrachloride and trimethylamine hydrochloride, in the proportion of two molecules of the former to one of the latter, were crystallized from a mixture of equal parts of alcohol and ether. The salt was obtained in colorless, semitransparent plates. The salt described above, $SeOCl_2.(CH_3)_3N.HCl$, was converted into the same compound by recrystallization from alcohol and ether without the presence of acid. Complete breaking down of the selenium oxychloride to selenium dioxide did not take place, one-half alone being changed. The relation between the two salts can be seen best by doubling the formula of the compound $SeOCl_2.(CH_3)_3N.HCl$.

$$SeOCl_2.SeOCl_2.2(CH_3)_3N.HCl.$$
$$SeOCl_2SeO_22(CH_3)_3N.HCl.H_2O.$$

Muthmann and Schäfer found that for each molecule of selenium dioxide there was a molecule of water present in the compound. The rule is followed here also. There is but one molecule of selenium dioxide and one of water.

Another step suggested itself, the complete breaking down of the selenium oxychloride to oxide and the formation of the salt $SeO_2(CH_3)_3N.HCl.H_2O$. An attempt was made to get this salt by crystallizing selenium dioxide and the chloride of trimethylamine from alcohol and ether. Only a small amount of salt was obtained, which proved to have the composition $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.

In making both of the chlorides, selenium dioxide and hydrochloric acid can be used instead of the chloride. The ease of preparation and the properties of the oxide render its use more advantageous.

The analyses of the two samples of the salt follow:

I. 0.2012 gram salt gave 0.0651 gram Se.

II. 0.1565 gram salt gave 0.0508 gram Se.

III. 0.2257 gram salt gave 0.2667 gram AgCl.

IV. 0.2103 gram salt gave 0.2486 gram AgCl.

	Calculated for $SeOCl_2.SeO_22(CH_3)N.HClH_2O$.	Found.			
		I.	II.	III.	IV.
Se	32.49	32.35	32.46	....	....
Cl	29.10	....	....	29.25	29.24

The Bromides.

A systematic search for the possible bromides was made. Selenium tetrabromide and trimethylamine hydrobromide, in varying proportions, were dissolved in hydrobromic acid and the solution evaporated to crystallization. Three different salts were formed. Special precautions were necessary to get the salts pure, as there was a great tendency for the two salts to crystallize together.

Salt of the Composition $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$.—Two molecules of selenium tetrabromide and one molecule of the bromide of trimethylamine were dissolved in dilute hydrobromic acid, and the solution evaporated to crystallization. On cooling, long red needles separated. These were removed, washed with absolute alcohol, and analyzed. This salt has attractive properties. It is stable in dry air and can be recrystallized from dilute hydrobromic acid, water, and alcohol. From hot saturated solutions in acid it separates as long, stout needles, sometimes 2 cm. in length. By slow evaporation, large, well-developed orthorhombic crystals of a deep-red color were obtained. The usual habit is a combination of prism, orthopinacoid, and basal plane. At times the pyramids and the orthodomes occur. This is the most stable of the bromides containing trimethylamine and selenium, and is the form in which the two halides tend to unite unless special precautions are taken. If crystallization takes place rapidly in a solution containing an excess of trimethylamine hydrobromide, this salt crystallizes out until the solution cools, when another compound is deposited.

There is no direct method of proving the presence of both selenium tetrabromide and selenium oxybromide in the compound, but all the facts are in accord with the formula given. The ratio of selenium to bromine is one to four. It could not, therefore, be a simple double halide containing selenium tetrabromide. And, further recognizing the tendency of the bromide of selenium to decompose, the above formula seems justified. As is generally admitted, the constitution of the double halides is not expressed by any such formula as $SeBr_4.2NH_4Br$. Accepting the explanation of their constitution advanced by Remsen,[1] in the formula given above, the $SeOBr_2$ means simply that all of the oxygen has not been replaced by bromine. A constitutional formula of such a salt can be written.

The analysis of the compound follows:

I. 0.3141 gram salt gave 0.0529 gram Se.
II. 0.3531 gram salt gave 0.0601 gram Se.
III. 0.2246 gram salt gave 0.3616 gram AgBr.
IV. 0.3281 gram salt gave 0.5277 gram AgBr.

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[1] This Journal, 11, 291.

	Calculated for $SeBr_4.SeGBr_2.2(CH_3)_3N.HBr$.	Found.			
		I.	II.	III.	IV.
Se	16.90	16.84	17.00	....	....
Br	68.51	....	....	68.44	68.43

Salt of the Composition $SeBr_4.2(CH_3)_3N.HBr$.—If a solution containing a large excess of trimethylamine hydrobromide in dilute hydrobromic acid is evaporated to crystallization, a dark, greenish-brown mass of fine needles mixed with the salt, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, is first deposited. If this solution is left to evaporate further in a desiccator, there appear, floating on the surface of the solution and scattered throughout the mass of green needles, large, perfectly formed, red octahedra modified by cube. These can be readily separated and the salt obtained pure. This salt proved to be the compound $SeBr_4.2(CH_3)_3N.HBr$, analogous to the ammonium, potassium, and rubidium double halides with selenium bromide. These also crystallize in octahedra. If selenium tetrabromide and trimethylamine hydrobromide, in the molecular proportions of one to two, are dissolved in dilute hydrobromic acid and the solution left to evaporate slowly, the salt is obtained generally mixed, however, with some of the green salt. It is impossible to get it from a hot, saturated solution. In this respect it differs from the potassium and ammonium salts of like composition. The analysis gave the following results:

I. 0.1589 gram salt gave 0.0183 gram Se.
II. 0.2969 gram salt gave 0.0339 gram Se.
III. 0.2718 gram salt gave 0.4501 gram AgBr.
IV. 0.1299 gram salt gave 0.2150 gram AgBr.

	Calculated for $SeBr_4.2(CH_3)_3N.HBr$.	Found.			
		I.	II.	III.	IV.
Se	11.65	11.52	11.42	....	....
Br	70.68	....	....	70.47	70.40

A third bromide was also obtained but never in pure condition. As stated above, when a solution containing selenium tetrabromide and a large excess of trimethylamine hydrobromide was evaporated, fine greenish-brown needles were obtained, mixed with the two salts described. Renewed effort failed to discover a method of getting this salt free from the other compounds. Under certain conditions the salt is very unstable, changing readily into the compound $SeBr_4.2(CH_3)_3N.HBr$. If a solution containing selenium tetrabromide and trimethylamine hydrobromide, in the proportion of one molecule of the former to three of the latter, is evaporated to crystallization, the salt crystallizes out in green needles or flakes, as long as the solution is hot. If an attempt is made to remove it, the crystals break up and change to a red powder. At times the salt was obtained in good condition after the solution had cooled to the temperature of the room. The movement of the beaker was sufficient to cause a partial change from the green needles to the red powder. An analysis of this mixture showed less bromine and more selenium than was required for the salt $SeBr_4.2(CH_3)_3N.HBr$. This was evidence that the green crystals and the red powder were not two forms of the same compound. The green needles were obtained at times in a stable form, but in this case always mixed with the other two salts. When an attempt was made to recrystallize the impure green salt from hydrobromic acid, it did not go into solution at once, but sank to the bottom of the vessel as a dark brown oil, which was slowly taken up by the acid. It is hoped that further work will clear up the nature of this compound.

Salt of the Composition $SeBr_4.2[(CH_3)_3N.HBr_2]$.—This salt was first prepared as the result of the action of bromine on the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. The oxy-salt was treated with bromine and concentrated hydrobromic acid and heated until solution took place. On cooling, a dark-red powder crystallized out. It was hoped in this way to replace the oxygen by bromine and to thus obtain the compound $SeBr_4.(CH_3)_3N.HBr$. The crystalline precipitate did not conduct itself, however, like a double halide of selenium and trimethylamine. It dissolved in water with evolution of bromine and, on evaporation to crystallization, the double salts above described were obtained. The study of the compound led to experiments on trimethylamine hydrobromide. This took up bromine in the same way as the double salt and was converted into the compound $(CH_3)_3N.HBr_2$. This evidently entered into combination with selenium tetrabromide to form a double salt. The salt can be obtained best in the following manner: Selenium tetrabromide and the bromide of trimethylamine in the molecular ratio of one to two are dissolved in dilute hydrobromic acid, and the solution evaporated till, on cooling, a salt will separate out. To the hot solution is added bromine. The salt crystallizes in well-formed, stout, needle-shaped crystals of a dark-red to grayish-black color. The surface color is like that of iodine, the powder is dark-red. The salt is very stable in dry air. It can be crystallized from hydrobromic acid containing bromine, and, if the solution is allowed to evaporate slowly, the salt is obtained in large clusters of octahedra grouped together. It gives off two atoms of bromine quantitatively, when dissolved in water. The analyses resulted as follows:

I. 0.2447 gram salt gave 0.0230 gram Se.
II. 0.3545 gram salt gave 0.0336 gram Se.
III. 0.1770 gram salt gave 0.1352 gram Br.
IV. 0.2242 gram salt gave 0.1713 gram Br.
V. 0.3074 gram salt gave 0.2770 gram I.
VI. 0.1392 gram salt gave 0.1245 gram I.

In analyses V and VI the iodine is that liberated by the free bromine plus that set free by the selenium dioxide. Deducting the latter and finding the equivalent in bromine we have:

V. 0.3074 gram salt gave 0.0585 gram free Br.
VI. 0.1392 gram salt gave 0.0263 gram free Br.

	Calculated for $SeBr_4.2[(CH_3)_3N.HBr_2]$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Se	9.42	9.39	9.48	....	....	....	....
Total Br	76.28	....	....	76.37	76.44	....	....
2 atoms Br	19.07	....	....	....	....	19.03	18.90

Salt of the Composition $SeBr_4.2[(CH_3)_3N.HBr_2].(CH_3)_3N.HBr$.—As a new kind of compound was obtained by crystallizing from solutions containing bromine, the effect of varying the proportions of the constituents was studied. In all cases, when the method described above was used, that is, crystallization from hot saturated solutions, the same compound, $SeBr_4.2[(CH_3)_3N.HBr_2]$, was obtained. But when a solution containing a large excess of trimethylamine hydrobromide (five molecules to one of selenium tetrabromide) and bromine was allowed to crystallize slowly, a double bromide was obtained, mixed with the compound $(CH_3)_3N.HBr_2$. The salt crystallizes in red crystals, which, in general appearance, resemble the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. These are easily separated from the mixture and thus obtained in pure condition. When the salt is dissolved in water, two atoms of bromine are liberated. This shows that but two molecules of the compound $(CH_3)_3N.HBr_2$ are present. The atomic ratio of selenium to bromine is one to nine. The selenium in the selenium tetrabromide requires four atoms of bromine. The two molecules of $(CH_3)_3N.HBr_2$ furnish four more. A molecule of trimethylamine hydrobromide would bring the number of halogen atoms up to nine. The analysis of the compound agrees with this composition.

I. 0.2175 gram salt gave 0.0170 gram Se.
II. 0.2260 gram salt gave 0.0379 gram Br.
III. 0.2115 gram salt gave 0.3653 AgBr..

	Calculated for $SeBr_4.2[(CH_3)_3.N.HBr_2].(CH_3)_3N.HBr$.	Found. I.	II.	III.
Se	8.04	7.81	....	....
2 atoms Br	16.33	....	16.70	....
Total Br	73.50	....	....	73.49

SALTS WITH DIMETHYLAMINE.

The Chlorides.

Salt of the Composition $2SeOCl_2.3(CH_3)_2NH.HCl$.—Following the method which was used with trimethylamine hydrochloride, two double salts containing selenium and dimethylamine were obtained. The salt $2SeOCl_2.3(CH_3)_2NH.HCl$ crystallized from a solution of two molecules of selenium tetrachloride or selenium dioxide and one of dimethylamine hydrochloride in strong hydrochloric acid. The usual habit of the crystals is a combination of a monoclinic prism with the basal planes. The salt is very soluble in water, alcohol, and hydrochloric acid, and deliquesces in the air. It melts when gently heated and remains liquid for a long time. It is insoluble in ether. A mixture of three parts of ether and one of alcohol was used to wash the salt in preparing it for analysis. The results of the analyses follow:

I. 0.2015 gram salt gave 0.0557 gram Se.
II. 0.2082 gram salt gave 0.0578 gram Se.
III. 0.2086 gram salt gave 0.0899 gram Cl.
IV. 0.1732 gram salt gave 0.0746 gram Cl.

	Calculated for $2SeOCl_2.3(CH_3)_2NH.HCl$.	Found.			
		I.	II.	III.	IV.
Se	27.57	27.64	27.76	....	....
Cl	43.24	....	....	43.10	43.07

Salt of the Composition $SeO_2.(CH_3)_2NH.HCl$.—This salt was found when the compound $3SeOCl_2.2(CH_3)_2NH.HCl$ was recrystallized from a mixture of alcohol and ether. To obtain it directly 5 grams of selenium dioxide and 3.7 grams dimethylamine hydrochloride were dissolved in the smallest quantity of water, to which a few drops of dilute hydrochloric acid were added. The solution evaporated over sulphuric acid to a thick sirup from which, after standing two months, the salt separated in stout colorless prisms. On account of its great solubility it was difficult to free it from the adhering mother-liquor. It is interesting to note that with dimethylamine a salt containing selenium dioxide is possible, while with trimethylamine such a compound does not exist. The transition to the ammonium salt, $2SeO_2.NH_4Cl.2H_2O$, is evident. The analysis follows:

I. 0.4291 gram salt gave 0.1735 gram Se.
II. 0.4140 gram salt gave 0.3144 gram AgCl.

	Calculated for $SeO_2(CH_3)_2NH.HCl$.	Found.	
		I.	II.
Se	41.06	40.44	....
Cl	18.38	....	18.80

The Bromides.

A series of mixtures containing selenium tetrabromide and dimethylamine hydrobromide in varying proportions was made, and the resulting salts studied. The compounds differed markedly from those formed by trimethylamine. In all cases there was a considerable quantity of a salt formed which crystallized in light red needles. It was like the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$ in color and crystal form, but, on examination, it proved to have the formula $SeBr_4.2(CH_3)_2NH.HBr$. The analogous compound containing trimethylamine is obtained only under special conditions, while the salt $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$ is the form in which selenium tetrabromide and trimethylamine hydrobromide tend to unite. Mixed with the salt $SeBr_4.2(CH_3)_2NH.HBr$, in the beakers containing an excess of selenium halide, were well-formed, black crystals of a rhombohedral habit. This was the salt $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$. A few green needles were formed in the solutions containing an excess of dimethylamine.

Salt of the Composition $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$.—This salt can be obtained in pure condition from a solution containing a large excess of selenium tetrabromide (five molecules to one of dimethylamine hydrobromide) in strong hydrobromic acid. The solution is evaporated to such a concentration that, on cooling, the salt separates. Obtained in this way, the salt crystallizes in diamond-shaped plates of a dark-brown color. If dilute hydrobromic acid is used, a large amount of the salt $SeBr_4.2(CH_3)_2NH.HBr$ is formed. Water decomposes it with precipitation of selenium. When left exposed to the air, this decomposition takes place slowly, and the salt gradually becomes red.

In the compound of selenium and trimethylamine which contains the largest percentage of selenium, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, the ratio of selenium to bromine is one to four. The same ratio exists in the dimethylamine salt containing the largest amount of selenium. But the fact that it is decomposed by water with the liberation of selenium, points to a different composition from that assigned to the trimethylamine salt. Some compound of selenium containing less bromine than the tetrabromide must be present, in order to have the ratio one of selenium to four of bromine. The compound Se_2Br_2 is known and, considering the instability of the tetrabromide, there is a possibility of the formation of the lower halide, and of its entering into combination to form a double salt. Further, the monobromide is decomposed by water, and selenium is precipitated and, as stated, the salt described acts in this way. The analyses for total selenium and for bromine point to the formula given to the salt. The determination of the selenium precipitated is further evidence of its correctness. When water acts on selenium monobromide the following reaction takes place:

$$2Se_2Br_2 + 2H_2O = 3Se + SeO_2 + 4HBr.$$

That is, three-fourths of the selenium is precipitated. Now, if $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$ is the correct formula for the salt under discussion (selenium monobromide is written SeBr for simplicity) then three-fourths of the selenium in the monobromide should be precipitated; that is, three-fourths of one-third or one-fourth of the total selenium. The analyses show that this is the case. The following results were obtained:

I. 0.2310 gram salt gave 0.0412 gram Se.

II. 0.4102 gram salt gave 0.0724 gram Se.

III. 0.2547 gram salt gave 0.0336 gram Se as SeO_2 in solution.

IV. 0.3688 gram salt gave 0.0487 gram Se as SeO_2 in solution.

V. 0.1995 gram salt gave 0.1443 gram Br.

VI. 0.2321 gram salt gave 0.1671 gram Br.

Analyses III. and IV. were of the selenium dioxide in solution. The difference between this selenium and the total amount gives that which was precipitated.

	Calculated for	Found.					
	$2SeBr_4.SeBr.3(CH_3)_2NH.HBr$.	I.	II.	III.	IV.	V.	VI.
Total Se	17.75	17.84	17.65	...	...	....	....
Precip'd Se	4.44	....	....	4.54	4.53	....	....
Br	71.91	....	....	...	...	71.83	71.99

Salt of the Composition $SeBr_4.2(CH_3)_2NH.HBr$.— This is the form in which the two halides tend to unite. The salt is obtained in pure condition by evaporating a mixture of one molecule of selenium bromide and two of dimethylamine hydrobromide in dilute hydrobromic acid. When this takes place slowly, bright red, prismatic needles are obtained, which are comparatively stable in the air. It is very remarkable that this salt crystallizes in a different system from all the other selenium compounds of analogous composition. The double bromides of selenium of the general formula $SeBr_4.2MBr$, namely those containing potassium, rubidium, ammonium, and trimethylamine, all crystallize in octahedra, while the dimethylamine compound crystallizes in monoclinic or triclinic prisms.

The salt was analyzed with the following results:

I. 0.2873 gram salt gave 0.0347 gram Se.
II. 0.2353 gram salt gave 0.0285 gram Se.
III. 0.3544 gram salt gave 0.6136 gram AgBr.
IV. 0.1496 gram salt gave 0.1102 gram Br.

	Calculated for $SeBr_4.2(CH_3)_2NH.HBr$.	Found. I.	II.	III.	IV.
Se	12.13	12.07	12.11	....	....
Br	73.73	....	....	73.67	73.66

A third bromide was formed, crystallizing in bright green needles like the trimethylamine compound, which could not be obtained in pure condition. It was obtained once in considerable quantity in beautiful crystals mixed with some fine, red needles. It was impossible to separate the two compounds mechanically, so a few drops of water were added to the beaker and the salt redissolved, with the intention of removing the green salt, as soon as it was formed. When the solution cooled, only the red salt appeared. The crystals were redissolved over and over again without removing them from the mother-liquor. When the crystallization took place the results varied without any apparent rule. At times a mixture of the red and green salts was obtained, at times the pure red, but never the green alone. Finally the exact conditions were discovered, and the salt was obtained in an apparent state of purity. It can be prepared as follows: One molecule of selenium dioxide, or tetrabromide, and six of dimethylamine hydrobromide are dissolved in concentrated hydrobromic acid, and the solution evaporated at a temperature just below the boiling-point, until a salt begins to separate out on the surface of the liquid. The beaker is now set in a warm place, and left undisturbed till the solution has cooled to 60° or 70°. A large mass of fine green needles with a metallic lustre will be found. These are removed to a porous plate and thus freed from the excess of acid. It is impossible to wash the compound, as it is readily decomposed with precipitation of selenium. If the crystals are not removed while the liquid is at the temperature mentioned, they will be contaminated by another salt, which appears as soon as the solution has cooled to the temperature of the room.

Analyses of samples of the salt prepared in this way gave results which agreed with one another, but not with any possible formula.

Salt of the Composition $SeBr_4.2[(CH_3)_2NH.HBr_2]$.—The salt was obtained in the same way as the analogous trimethylamine compound. It crystallizes in dark-red needles and is best obtained from a hot saturated solution. Its appearance and properties are like those of the corresponding salt containing trimethylamine. The following analyses were made:

I. 0.1953 gram salt gave 0.1541 gram Br.
II. 0.1847 gram salt gave 0.1453 gram Br.
III. 0.2552 gram salt gave 0.0498 gram free Br.
IV. 0.2374 gram salt gave 0.0469 gram free Br.
V. 0.3196 gram salt gave 0.0314 gram Se.
VI. 0.2044 gram salt gave 0.0200 gram Se.

	Calculated for $SeBr_4.2[(CH_3)_2NH.HBr_2]$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Total Br	78.95	78.90	78.67	....	....	....	....
2 atoms Br	19.74	....	....	19.52	19.78	....	....
Se	9.74	....	....	....	....	9.88	9.78

Salt of the Composition $SeBr_4.2[(CH_3)_2NH.HBr_2].(CH_3)_2NH.HBr$.—A salt of this formula was obtained from a solution of one molecule of selenium tetrabromide and six of dimethylamine hydrobromide in strong hydrobromic acid. The solution was evaporated until a salt appeared on the surface of the liquid. Bromine was then added. On cooling, long prismatic crystals of a deep maroon color were deposited. The salt has a strong crystallizing force; the prismatic faces are well developed and possess a high lustre. It is perfectly analogous in composition to the trimethylamine salt, although quite different in appearance. It will be remembered that the compounds $SeBr_4.2(CH_3)_3N.HBr$ and $SeBr_4.2[(CH_3)_3N.$

$HBr_2].(CH_3)_3N.HBr$ are obtained only by spontaneous evaporation. The dimethylamine salts of similar composition are formed with ease in hot solutions. They also crystallize in entirely different forms in different crystalline systems.

The salt gave the following figures when analyzed :

I. 0.4419 gram salt gave 0.0367 gram Se.
II. 0.3143 gram salt gave 0.0258 gram Se.
III. 0.3077 gram salt gave 0.0519 gram free Br.
IV. 0.3075 gram salt gave 0.0517 gram free Br.
V. 0.1972 gram salt gave 0.1524 gram Br.
VI. 0.2679 gram salt gave 0.2070 gram Br.

	Calculated for $SeBr_4.2[(CH_3)_2NH.HBr_2](CH_3)_2NH.HBr$.	Found. I.	II.	III.	IV.	V.	VI.
Se	8.42	8.31	8.20	....	....	....	....
2 atoms Br	17.07	....	....	16.86	16.82	....	....
Total Br	76.86	....	....	....	....	77.23	77.26

Note.—Throughout the investigation the double salts were made by using selenium tetrachloride and tetrabromide, as the available supply of selenium was in these forms. It was found that selenium dioxide dissolved in the halogen acids served the purpose just as well. The oxide was made by treating selenium with concentrated nitric acid, evaporating to dryness, and subliming the residue.

Conclusion.

The double salts which have been described exhibit such complexity of structure that they cannot be rightly grouped under the class of doube halides, nevertheless it is interesting to note that with one exception the number of molecules of basic halide is never in excess of the number of halogen atoms combined with the selenium. The salts thus obey Professor Remsen's law[1] and can be explained by assuming the presence of a bivalent halogen group —$(Cl = Cl)$—. The one exception mentioned is the compound $SeO_2.(CH_3)_2NH.HCl$. This is not a double halide at all, and, therefore, is excluded from the generalization.

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[1] This JOURNAL, 11, 291.

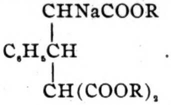
Contributions from the Chemical Laboratory of the University of Nebraska.

I.—ON PHENYLGLUTARIC ACID AND ITS DERIVATIVES.

BY S. AVERY AND ROSA BOUTON.

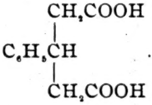
The alkyl succinic and glutaric acids have of late been a favorite subject with investigators. During the past few years Auwers, Perkin, and others have increased our knowledge of these compounds to a marked degree. At the same time the corresponding aromatic compounds have been but slightly investigated. We have accordingly entered upon the study of these acids, hoping to widen our knowledge of the subject in general, and especially to determine the influence of the phenyl group on melting-points and the formation of anhydrides.

In the course of his investigation on the addition of sodium acetoacetic ether and of sodium malonic ether to unsaturated ethers, Michael obtained by the action of sodium malonic ether on cinnamic ether an addition-product of the formula,



$$\begin{array}{rl} & CHNaCOOR \\ & | \\ C_6H_5 & CH \\ & | \\ & CH(COOR)_2 \end{array} .$$

When this compound is saponified and heated it yields β-phenylglutaric acid,



$$\begin{array}{rl} & CH_2COOH \\ & | \\ C_6H_5 & CH \\ & | \\ & CH_2COOH \end{array} .$$

The following description is given: "Schräg[1] abgestumpfte Prismen aus Benzol, Schmelzp. 137°.5–138°.5. Unlöslich in Wasser, wenig löslich in Benzol, leicht in Alkohol und Essigäther." The results of our investigations show that Professor Michael did not obtain the acid in a perfectly pure condition. He did not investigate it further than to make and analyze a silver salt, as he very kindly informed us in a private communication. As a preliminary experiment, carried out according to his method, failed to give a satisfactory yield, we endeavored to find a better method.

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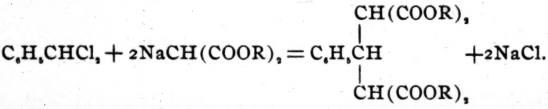
[1] J. prakt. Chem. [2], **35**, 352.

EXPERIMENTAL PART.

The Action of Benzal Chloride on Sodium Malonic Ether.

Pure benzal chloride was added to sodium malonic ether in alcoholic solution (2 molecules) in the hope of obtaining benzaldimalonic ether according to the equation,



$$C_6H_5CHCl_2 + 2NaCH(COOR)_2 = C_6H_5\overset{\displaystyle CH(COOR)_2}{\overset{|}{\underset{\underset{\displaystyle CH(COOR)_2}{|}}{CH}}} + 2NaCl.$$

Benzaldimalonic ether would readily yield β-phenylglutaric acid by saponification and loss of carbonic anhydride. The expected reaction, however, did not take place. On distilling in a vacuum the products of the reaction, about half of the distillate proved to be malonic ether. The rest of the distillate boiled at about 250°, at a pressure of 50 mm., and proved to be benzalmalonic ether. Evidently the reaction is to be expressed by the following:

$$C_6H_5CHCl_2 + 2NaCH(COOR)_2 = C_6H_5CH{=}C(COOR)_2 + \\ CH_2(COOR)_2 + 2NaCl.$$

It is of interest to note in this connection that, while Guthzeit and Dressel[1] obtained methylenedimalonic ether by the action of methylene iodide on sodium malonic ether, and Perkin[2] obtained similar results, using methylene chloride, Auwers[3] was unable to obtain an analogous product when working with chloracetol.

Condensation of Benzalmalonic Ether with Sodium Malonic Ether. Formation of Benzaldimalonic Ether.

A quantity of benzalmalonic ether was made according to the method of Classen and Crismer[4] by condensing benzaldehyde with malonic ether. Equivalent quantities of benzalmalonic ether and sodium malonic ether were brought together in alcoholic solution. The mixture became hot and changed to a gelatinous mass which, on treating with dilute sulphuric acid, gave a heavy oil. This oil decomposed considerably on distilling in vacuum, hence benzaldimalonic ether could not be obtained in a pure condition. That the oil just described consists principally of this ether follows from the fact that it gives an excellent yield of β-phenylglutaric acid.

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[1] Ann. Chem. (Liebig), **256**, 174.

[2] J. Chem. Soc. (London), **59**, 992.

[3] Ber. d. chem. Ges., **28**, 1130.

[4] Ann. Chem. (Liebig), **218**, 132.

Saponification of Benzaldimalonic Ether. Formation of β-Phenylglutaric Acid.

The oil just described was saponified with a solution of barium hydrate. On acidifying, an oily mass was obtained. This product, when heated above its melting-point, evolved carbonic anhydride, but gave no crystalline product. Similar results were obtained when alcoholic potash was used for saponifying. When the oil was saponified by boiling with sulphuric acid diluted with 2 volumes of water, a resinous mass was formed, but on pouring off the hot liquid and cooling, crystals were deposited. Protracted boiling with hydrochloric acid failed to effect complete saponification; hence we tried the action of hydrobromic acid. The oil was mixed with ten times its volume of strong hydrobromic acid and heated in a flask with return-condenser for twenty-four hours. Carbonic anhydride and ethyl bromide were evolved. The solution was now evaporated to dryness on the water-bath. The residue was extracted with boiling water. On concentrating the aqueous solution a white crystalline product was obtained which, after 2 or 3 crystallizations from hot dilute hydrochloric acid, melted sharply at 140°. It formed glistening plates soluble in water, alcohol, ether, and chloroform; scarcely soluble in benzene; insoluble in petroleum ether. A combustion gave the following:

	Calculated for $C_{11}H_{12}O_4$.	Found.
C	63.46	63.22
H	5.77	6.05

It will be noticed that the properties just given do not entirely agree with the properties of Michael's acid. The compounds are, however, identical, as we obtained the same substance by treating sodium malonic ether with cinnamic ether.

The difficulties in preparing it by the latter method disappear when the condensation-product without previous distillation is saponified with hydrobromic acid. In this way we prepared a quantity of the pure acid, obtaining seventy per cent. of the amount that quantitative reactions should afford, calculated from the ethers used in the preparation.

Salts of β-Phenylglutaric Acid.

Silver salt.—Made by neutralizing the acid with ammonia and precipitating with silver nitrate. Slightly soluble in hot water.

0.2651 gram of the substance gave 0.1350 gram metallic silver.

	Calculated for $C_{11}H_{10}O_4Ag_2$.	Found.
Ag	51.16	50.93

Barium salt.—Made by neutralizing a solution of the acid with barium hydrate. Precipitated out of the aqueous solution by alcohol. Glistening, white precipitate. Easily soluble in water. The salt was dried for analysis by heating on a water-bath.

0.1104 gram salt gave 0.0686 gram $BaSO_4$.

	Calculated for $C_{11}H_{10}O_4Ba.2H_2O$.	Found.
Ba	36.14	36.36

Copper salt.—Made by neutralizing the acid with freshly precipitated copper oxide. Green crystalline precipitate; scarcely soluble in water.

0.0884 gram salt dried on a water-bath gave 0.0185 gram metallic copper.

	Calculated for $C_{11}H_{10}O_4Cu.2H_2O$.	Found.
Cu	20.76	20.927

The barium and copper salts give off water, when heated to a higher temperature, before decomposition sets in.

The lead salt resembles the silver salt. The sodium, potassium, and ammonium salts are very easily soluble in water.

β-Phenylglutaric Anhydride.

This anhydride is made by heating the acid above its melting-point, or by treating the acid with acetyl chloride. The latter method gives the better yield. Excess of acetyl chloride is evaporated off on the water-bath. The residue is washed with petroleum ether and dissolved in hot benzene. Petroleum ether is now added till the solution begins to be cloudy. On cooling, the anhydride separates out in the form of glistening white plates; melting-point 105°; soluble in benzene, chloroform, and ether; insoluble in petroleum ether; scarcely affected by cold water; slowly converted into the acid by boiling; instantly changed by alkalies to salts of the acid.

0.2605 gram gave 0.6639 gram CO_2, and 0.1248 gram H_2O.

	Calculated for $C_{11}H_{10}O_3$.	Found.
C	69.47	69.50
H	5.26	5.32

β-Phenylglutaranilic acid.—The anhydride just described reacts almost quantitatively with aniline in benzene solution forming the anilic acid. Recrystallized out of dilute alcohol, the anilic acid melts at 168°. A silver salt of this acid was analyzed.

0.1842 gram of the salt gave 0.0508 gram silver.

	Calculated for $C_{17}H_{16}O_3NAg$.	Found.
Ag	27.67	27.57

β-Phenylglutaranil.—This anil is readily made by heating the anilic acid in a test-tube over the open flame. Crystallized from alcohol, it forms glistening white needles, which melt at 223°.

β-Phenylglutar-p-tolilic acid.—This acid was made by the action of *β*-phenylglutaric anhydride on *p*-toluidine; melting-point 154°–155°.

0.2312 gram acid gave 9.7 cc. nitrogen. T = 20°.1. Bar. = 739 mm.

	Calculated for $C_{18}H_{19}O_3N$.	Found.
N	4.71	4.66

Silver salt.—

0.2165 gram salt gave 0.0575 gram silver.

	Calculated for $C_{18}H_{18}O_3NAg$.	Found.
Ag	26.67	26.55

Comparison of the Melting-points of β-Phenylglutaric Acid and Its Derivatives with those of the Corresponding Benzylsuccinic Acid and Its Derivatives.

We made the benzylsuccinic acid by the method of Bischoff and Mintz.[1] The anhydride and its derivatives with aromatic bases were prepared by methods previously given in this paper. The results are shown in the following table:

β-Phenylglutaric acid,	140°
β-Phenylglutaric anhydride,	105°
β-Phenylglutaranilic acid,	167°–168°
β-Phenylglutaranil,	223°
β-Phenyl-*p*-tolilic acid,	154°–155°
Benzylsuccinic acid,	161°
Benzylsuccinic anhydride,	99°
Benzylsuccinanilic acid,	157°–159°
Benzylsuccinanil,	indistinct
Benzylsuccin-*p*-tolilic acid,	165°

Action of β-Phenylglutaric Anhydride on Phenol in the Presence of Sulphuric Acid.

The anhydride, when heated with phenol and sulphuric acid, gives a brownish coloration. This sulphuric acid solution, when diluted with a large excess of water, is nearly colorless. On adding an alkali a blue-green coloration is produced. The color disappears on the addition of an acid. The coloring-matter has not been isolated.

Action of Fuming Sulphuric Acid on β-Phenylglutaric Anhydride.

A few grams of the anhydride were dissolved in fuming sulphuric acid. After heating for a few minutes on the water-bath the solution was poured into ice-water. In this way a beautiful crystalline product was obtained that melted at 153°. The crystals contained no sulphur. The amount of material was too small to permit of further investigation than the making and analyzing of a silver salt.

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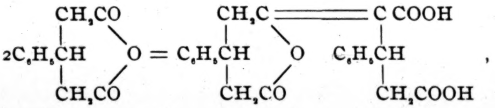
[1] Ber. d. chem. Ges., 23, 653.

0.1736 gram salt gave 0.0632 gram silver.

	Calculated for $C_{22}H_{18}O_6Ag_2$.	Found.
Ag	36.33	36.40

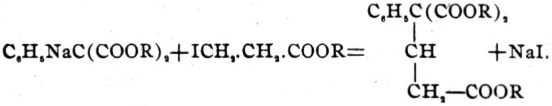
If we assume that 2 molecules of the anhydride condense in the manner indicated by the following equation,



we arrive at the formula of an acid whose silver salt would correspond in composition to the silver salt above given.

The Action of β-Iodopropionic Ether on Sodium Phenylmalonic Ether.

We heated these substances in alcoholic solution supposing that they would react in the following manner:



$$C_6H_5NaC(COOR)_2 + ICH_2.CH_2.COOR = \begin{array}{c} C_6H_5C(COOR)_2 \\ | \\ CH \\ | \\ CH_2—COOR \end{array} + NaI.$$

A tricarboxylic ether of this structure would in all probability readily yield the unknown α-phenylglutaric acid. We found, however, that the ethers react as follows:

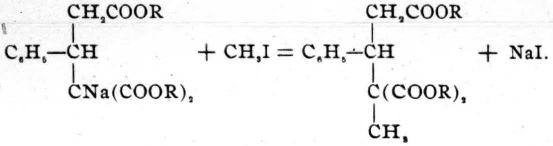
$$C_6H_5NaC(COOR)_2 + ICH_2CH_2COOR = C_6H_5CH(COOR)_2 \\ + CH_2{=}CH—COOR + NaI.$$

We hope to prepare α-phenylglutaric acid by another method.

II.—ON α-METHYL-β-PHENYLGLUTARIC ACID.

BY S. AVERY AND MARY L. FOSSLER.

In preparing this acid we met with unexpected difficulties. Sodium methylmalonic ether and cinnamic ether were heated in alcoholic solution in the usual way. On saponifying with hydrobromic acid an oily substance was obtained. We did not succeed in obtaining a crystalline product. We next heated sodium malonic ether with cinnamic ether, neutralized with hydrochloric acid, then washed and dried the oil carefully. As one of us and Miss Bouton[1] have shown in the previous paper, this oil consists principally of phenylpropanetricarboxylic ether. This product was treated with sodium alcoholate and methyl iodide. The expected reaction was as follows:



$$C_6H_5-\overset{\displaystyle CH_2COOR}{\underset{\displaystyle CNa(COOR)_2}{CH}} + CH_3I = C_6H_5-\overset{\displaystyle CH_2COOR}{\underset{\underset{\displaystyle CH_3}{\displaystyle C(COOR)_2}}{CH}} + NaI.$$

All attempts to obtain a crystalline product by saponification and heating resulted in failure. After a number of unsuccessful attempts, we finally succeeded in preparing a small quantity of α-methyl-β-phenylglutaric acid by the following method: α-Methylcinnamic acid was prepared by Perkin's[2] method and converted into the methyl ether. This was condensed with sodium malonic ether. When acidified the condensation-product yielded methylphenylpropanetricarboxylic ether, and, on saponification with caustic potash, the corresponding acid. Neither of these compounds was isolated in pure condition. The impure acid was distilled over an open flame, carbonic anhydride, water, and an oil passing off. This oil, presumably an impure anhydride of α-methyl-β-phenylglutaric acid, dissolved for the most part in ammonia.

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[1] Page 509.

[2] J. Chem. Soc. (London), 1877, 789.

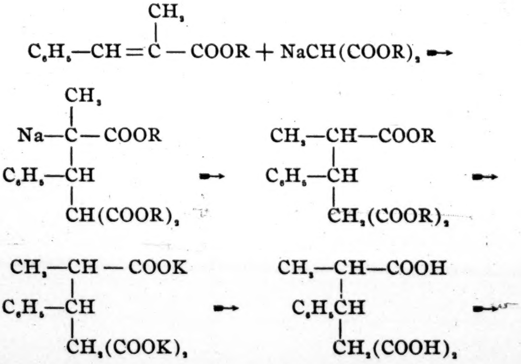
To the solution of the ammonium salt copper sulphate was added, when a green precipitate was formed. This was washed with water, alcohol, and ether; then suspended in water and decomposed with hydrogen sulphide. On evaporating the aqueous solution, crystals separated out. These were repeatedly recrystallized from benzene till the melting-point remained constant at 122°. They formed flaky, white plates; soluble in alcohol, ether, chloroform, and hot benzene; insoluble in petroleum ether. The greater part of the small quantity that remained after the repeated crystallizations was used in making a silver salt.

0.1122 gram of salt gave 0.0555 gram silver.

	Calculated for $C_{12}H_{12}O_4Ag_2$.	Found.
Ag	49.46	49.46

On treating the acid with acetyl chloride a substance resembling an anhydride was formed. The amount of material did not permit of our obtaining the anhydride in a pure condition.

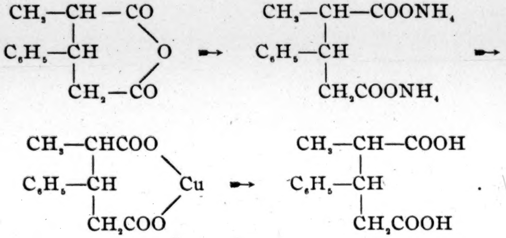
The reactions by which the acid was prepared may be indicated as follows:



$$C_6H_5—CH = \overset{\displaystyle CH_3}{\overset{|}{C}} — COOR + NaCH(COOR)_2 \rightarrow$$

$$\begin{array}{l} \quad\;\, CH_3 \\ \quad\;\;\; | \\ Na—C—COOR \\ \quad\;\;\; | \\ C_6H_5—CH \\ \quad\;\;\; | \\ \quad\;\, CH(COOR)_2 \end{array} \rightarrow \begin{array}{l} CH_3—CH—COOR \\ \qquad\;\;\; | \\ C_6H_5—CH \\ \qquad\;\;\; | \\ \qquad\; CH_2(COOR)_2 \end{array} \rightarrow$$

$$\begin{array}{l} CH_3—CH—COOK \\ \qquad\;\;\; | \\ C_6H_5—CH \\ \qquad\;\;\; | \\ \qquad\; CH_2(COOK)_2 \end{array} \rightarrow \begin{array}{l} CH_3—CH—COOH \\ \qquad\;\;\; | \\ C_6H_5CH \\ \qquad\;\;\; | \\ \qquad\; CH_2(COOH)_2 \end{array} \rightarrow$$



We lost the greater part of the acid on recrystallizing. A glance at the formula will show the presence of two asymmetric carbon atoms. The oily condition of the acid and the difficulty in purifying probably arose from the presence of stereoisomers.

We shall investigate this subject further as well as the isomers and homologues of the compounds described.

REVIEWS.

Methods for the Analysis of Ores, Pig Iron, and Steel in Use at the Laboratories of Iron and Steel Works in the Region about Pittsburg, Pa. Together with an Appendix containing various special methods of analysis of ores and furnace products. Contributed by the chemists in charge, and edited by a Committee of the Chemical Section, Engineers' Society of Western Pennsylvania. Chemical Publishing Co., Easton, Pa. 1898. iv + 133 pp. Price $1.00.

In the circular first sent out by the committee a request was made that the chemists addressed shall furnish a full description of the methods used in the daily laboratory work for the determination of the following substances :

In Ores—Silica, iron, phosphorus, manganese.

In Pig Iron—Silicon, sulphur, phosphorus, manganese.

In Steel—Carbon (by combustion), sulphur, phosphorus, manganese, nickel.

The report gives the methods in use in 16 different laboratories. The report was at first published by the Engineers' Society of Western Pennsylvania, but the edition having been exhausted it is republished in a more convenient and more generally accessible form.

The exigencies of the iron and steel laboratories, which require an enormous number of analytical determinations, have caused the development of many rapid methods, some of which are at the same time very accurate. The present work, from its nature, gives a compilation of those methods which have stood the test of actual use and of the comparisons which come with fierce business competition. The value of such a book is evident. The descriptions of methods are, of course, concise, and repetition is avoided by constant reference to published methods, especially to those in Blair's Analysis of Iron, but those engaged in this field of work will find in the study of the book very many useful suggestions.

W. A. N.

THE CALORIFIC POWER OF FUELS. Founded on Scheurer-Kestner's Pouvoir Calorifique des Combustibles, with the addition of a very full collection of tables of heats of combustion of fuels, solid, liquid, and gaseous, to which is also appended the report of the Committee on Boiler Tests of the AMERICAN SOCIETY OF MECHANICAL ENGINEERS (December, 1897); tables of constants used. By HENRY POOLE, F.C.S., member of the Society of Chemical Industry; the American Chemical Society; the American Society of Civil Engineers; the American Society of Mechanical Engineers; etc. First edition. First thousand. 8vo. Cloth. 40 figures, 279 pages. $3.00. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1898.

After discussing units, definitions, and thermometers, the various formulæ for calculation of the calorific power from the chemical composition are treated in detail. The statement that these formulæ are more applicable to cokes and hard coals rather than to bituminous, would seem to be open to question. The Berthier (litharge) test is not given the credit to which it is entitled.

The next 3 chapters deal with the principal calorimeters, that of Mahler and its method of working being described sufficiently minutely to be used in the laboratory; the discussion of the errors and corrections is especially full. The chapters upon the three kinds of fuel would hardly appear to be "adapted to American methods and data," as with few exceptions, the analyses and tests are those obtained in European practice.

The remaining chapters are devoted to the determination of the calorific power of fuel burned under a steam boiler; these are clearly written and unusually complete. The methods of sampling gases described are too expensive and troublesome to find universal adoption.

In addition to the report indicated on the title-page, the appendix contains many useful tables. Especially noteworthy are those giving the analysis and calorific power of fuels from all parts of the world.

The work will be of value to everyone interested in the application of fuel. Its value would have been increased to the investigator had it contained more references to the original sources. A. H. GILL.

THE TUTORIAL CHEMISTRY. Part I, Non-metals; Part II, Metals. By G. H. BAILEY, D.Sc., London, Ph.D., Heidelberg, Lecturer in Chemistry in the Victoria University. Edited by WILLIAM BRIGGS, M.A., F.C.S., F.R.A.S., Principal of University Correspondence College. London: W. B. Clive, University Correspondence College Press. Hinds & Noble, 4 Cooper Institute, New York.

The London University Correspondence College is an association of teachers who fit students by correspondence for the London University examinations. We might think that instruction given in this way would be superficial or mere cramming. An examination of these two volumes shows that Dr. Bailey, whose research work is favorably known to all chemists, has given an admirable condensed presentation of the facts and theories of inorganic chemistry, and shows furthermore that systematic laboratory work and a great deal of it is demanded.

In the first volume, on non-metals, all experiments are described in the text and each chapter closes with questions for self-examination; the last chapter treats of chemical calculations with examples and problems.

The treatment of the second volume, on metals, is original; the first 100 pages are given to physical chemistry under the following heads: Determination of atomic weight, relations between the atomic weights, constitution of gaseous compounds, constitution of liquid compounds, solution. The author admits in the preface that this section "may appear somewhat difficult to a chemist in his second year of study," but he believes that no real obstacle will be met, provided the student has already had some experience in dealing with physical problems. A perusal of this part of the book leads the reviewer to share this belief, as Dr. Bailey's presentation of the subject is very clear and as simple as possible. The remaining 200 pages are given to the chemistry of the metals, directions for experiment being relegated to the appendix, which also includes a few pages on crystallography and spectrum analysis.

Dr. Bailey's work is cordially recommended to those who wish a concise text-book of inorganic chemistry, thoroughly up to date in matter and treatment, but the chapters on physical chemistry would be valueless to many American college students of chemistry, as some knowledge of physics is essential to its study. E. R.